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JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Orders of Isomerism among Homologous Paraffins. By SIMA M. LOSANITSCH (*Ber.*, 1897, 30, 1917—1926).—The author has elaborated a table which indicates the number of possible isomerides for each member of the methane series from CH_4 to $\text{C}_{20}\text{H}_{42}$. By a system of analysis which is explained in the paper, the number of isomerides belonging to each order of isomerism has been calculated and recorded in separate columns of the table. M. O. F.

The Formation of Natural Petroleum and the Spontaneous Polymerisation of Hydrocarbons. By CARL ENGLER (*Ber.*, 1897, 30, 2358—2365).—The supposition that the natural petroleums have, as a rule, been formed by the distillation under pressure of fats derived from animal organisms, accounts for the fact that these oils contain extremely little nitrogen. It, however, does not appear to account for the high molecular weight, boiling point, and specific gravity of the constituents of the oil, since in all experiments which have been made on the distillation of fats, the product has consisted mainly of low boiling, light hydrocarbons. The author proposes to ascribe this to the gradual polymerisation of the light hydrocarbons which form the first product of the distillation, and has examined a number of distillates derived from various sources for evidence in favour of such a gradual change in density. Samples of Galician petroleum were found to increase in specific gravity by 0.0011—0.0015 in about three weeks, whilst petroleum from Java increased by 0.01 in a few days. Similar results were obtained with distillates from coal tar and brown-coal tar. Finally, the fractions obtained by the distillation of fats under pressure were

proved to behave in a similar manner. The sp. gr. of one set of samples increased by about 0.002 in a month, whilst five other specimens which had been preserved for nine years had increased in sp. gr. during that time by 0.016. It appears probable, therefore, that the comparatively high specific gravity of the constituents of natural petroleum has been acquired in this way during the extended period which has elapsed since the first production of the material. A. H.

Formation of Olefines, Naphthenes, and Benzene Hydrocarbons by the Distillation of Fats under Pressure. By CARL ENGLER and TH. LEHMANN (*Ber.*, 1897, 30, 2365—2368).—The distillate obtained by heating fish oil under pressure contains about 37 per cent. of olefines, which will combine with bromine or sulphuric acid. These are apparently mixtures of the various members of the series from hexylene up to nonylene. The presence of naphthenes could not be proved with certainty, but the composition of the various fractions after the removal of olefines and benzene derivatives appeared to point to the presence of small amounts of these hydrocarbons along with the paraffins. The benzene derivatives were recognised by conversion into their nitro-compounds, benzene, toluene, metaxylene, mesitylene, and pseudocumene being all detected. A. H.

Purification of Commercial Acetylene. By GEORG LUNGE and EDUARD CEDERCREUTZ (*Zeit. angew. Chem.*, 1897, 651—655).—(See this vol., ii, 54.)

Rutheniocyanides. By JAS. LEWIS HOWE (*J. Amer. Chem. Soc.*, 1896, 18, 981—987. Compare Abstr., 1894, ii, 386).—A better yield of potassium rutheniocyanide, $K_4RuC_6N_6 + 3H_2O$, is obtained when potassium cyanide is fused with potassium ruthenionitrosochloride than when the ammonium salt is used. A good yield may also be obtained by fusing ruthenium with potassium hydroxide, dissolving the melt in water, and then boiling with potassium cyanide. Other methods were tried, but the amount of rutheniocyanide formed was extremely small. A number of reactions of rutheniocyanides are enumerated. Lead acetate gives a fine, white precipitate, soluble in nitric acid; silver nitrate, a white, curdy precipitate, insoluble in ammonia or nitric acid; ferric chloride, a rich purple precipitate which is soluble in water, but is reprecipitated by salts or alcohol; ferrous sulphate, a pale green precipitate changing to violet, and copper sulphate, a pale green, flocculent precipitate. Bromine changes the solution to a dark red; nitric acid has no action in the cold, but on gently heating reddens the solution.

Two methods of purification applicable to such portions of rutheniocyanides as cannot be separated by crystallisation are given.

A substance crystallising in thick, straw-coloured, hexagonal plates was obtained by boiling potassium ruthenionitrosochloride with a strong solution of potassium cyanide; this compound is still under investigation.

Barium rutheniocyanide, $Ba_2RuC_6N_6 + 6H_2O$, obtained from the potassium salt, crystallises in pale, straw-coloured, diamond-shaped

monoclinic crystals slightly soluble in cold water. It loses $5\frac{1}{2}\text{H}_2\text{O}$ at 100° , and the remaining $\frac{1}{2}\text{H}_2\text{O}$ at about 200° . J. J. S.

Does the Volume of a Liquid Change in Consequence of Alcoholic Fermentation? By TÁMAS KOSUTÁNY (*Landw. Versuchs-Stat.*, 1897, 49, 173—183).—The results of the author's experiments indicate that the volume of a saccharine liquid is not altered by fermentation, and that the volume of the sugar which is decomposed is the same as that of the alcohol produced. It is probable that the volume of the carbonic anhydride formed, considered as a liquid, is the same as that of the decomposed sugar and the newly formed alcohol; that is to say, 1 vol. sugar = 1 vol. alcohol = 1 vol. liquid carbonic anhydride. N. H. J. M.

Preparation of Ether Free from Alcohol. By P. FRITZSCHE (*Zeit. anal. Chem.*, 1897, 36, 298—302).—Ethyl hydrogen sulphate, when heated with sulphuric acid at $130\text{--}140^\circ$, yields only traces of ether, whilst at higher temperatures sulphurous anhydride and ethylene are evolved. (Compare Graham, *Annalen*, 1850, 75, 108, and Buignet, *J. Pharm.*, 1850, [iii], 18, 130.) If the mixture is diluted with 10 per cent. of water, small quantities of ether and alcohol are obtained, and if a larger proportion of water is used more ether is obtained, but it is always mixed with large quantities of alcohol. When the amount of water exceeds 50 per cent., ether is no longer formed, and alcohol is the sole product. The author recommends the following method for the preparation of ether free from alcohol. Four flasks, A, B, C and D, are so connected that the gas which is evolved from A passes through a tube leading nearly to the bottom of B, the other flasks are connected in a similar manner, and D in its turn is connected with a good condenser. An equal quantity of ethyl hydrogen sulphate or mixture of alcohol and sulphuric acid is placed in each flask, water is added to A, B and C so that A contains 33 per cent. of water, B 22 and C about 10 per cent. A is strongly heated and B gently, C and D are gently heated as the ether begins to distil over from B. The contents of D should not increase to any appreciable extent, C should show a slight, and B a considerable, increase. When A yields no more vapours, its contents are removed and replaced by those of B. Similarly, those of C are passed into B, and those of D into C, a fresh supply of ethyl hydrogen sulphate being placed in D. In the usual preparation of ether by running alcohol into a heated mixture of alcohol and sulphuric acid, the vapours which pass over can be freed from alcohol by making them pass through a small flask containing ethyl hydrogen sulphate or even sulphuric acid. J. J. S.

Manufacture of Ethyl Hydrogen Sulphate from Gases Containing Ethylene. By P. FRITZSCHE (*Zeit. anal. Chem.*, 1897, 36, 303—306).—The gas, coal gas or gas from coke ovens, for example, is freed from tar, ammonia, benzene, and carbon bisulphide and then dried. The drying and removal of condensation products is accomplished by treating the gas with dilute (under 80 per cent.) sulphuric acid at $70\text{--}80^\circ$. By this means, homologues of ethylene are also removed. The gas is then heated to $110\text{--}120^\circ$ and passed

into the absorption apparatus. This consists of scrubbers kept at $110-120^{\circ}$, and filled with acid-proof stones over which sulphuric acid trickles. Four of five of these are connected in series, the fresh acid being always run into the last scrubber where the gas makes its exit: after leaving this last scrubber, the acid is pumped to the top of the next and so on, until it contains 50—60 per cent. of ethyl hydrogen sulphate. It can then be used for the manufacture of alcohol or ether.

J. J. S.

Nitropropylic Alcohol. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, 16, 189—192).—Twenty-five grams of nitroethane are added to a mixture of formaldehyde of 35 per cent. (30 grams) with an equal volume of water; several small pieces of potassium hydrogen carbonate are thrown in, and the mixture is vigorously shaken. The action proceeds slowly, the temperature rises some 30° , and the nitroethane gradually disappears. The products of several experiments are united, extracted with ether, and the ether evaporated; if the residue, after drying in a vacuum over sulphuric acid, is placed in a mixture of ice and salt, the greater part of the nitroisobutylic glycol (Abstr., 1896, i, 4) separates in a crystalline form. The residual liquid is subjected to repeated distillation under diminished pressure, when *β -nitropropylic alcohol*, $\text{NO}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, is obtained in the form of a colourless oil boiling at $120-122^{\circ}$ under 32 mm. pressure; its sp. gr. = 1.209 at 6° ; it is readily soluble in ether, or in alcohol and ether. Phosphorus pentachloride converts it into *nitropropylic chloride*, $\text{NO}_2\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl}$, boiling at $172-173^{\circ}$.

J. J. S.

Nitro-Alcohols. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, 16, 193—207. Compare Abstr., 1896, i, and preceding abstract).—

I. Nitroalcohols containing C_3 .

β -Nitropropylic alcohol, $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NO}_2$, and *β -nitroisopropylic alcohol*, $\text{NO}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, have already been described. *γ -Nitropropylic alcohol*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2$, is obtained by the action of silver nitrite on trimethylenic iodohydrin (next abstract). It is a colourless, somewhat viscous liquid, having a feebly pungent odour, and is readily soluble in water, alcohol or ether. Its sp. gr. = 1.175 at 13° , and it distils at $138-140^{\circ}$ under 32 mm. pressure. It readily condenses with piperidylcarbinol, $\text{C}_5\text{H}_{10}\cdot\text{N}\cdot\text{CH}_2\cdot\text{OH}$, yielding a compound, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_5\text{H}_{10}$, which crystallises in large needles melting at $70-71^{\circ}$. The *acetate*, $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$, is a colourless liquid boiling at $140-142^{\circ}$ under 38 mm. pressure. Its sp. gr. = 1.191 at 16° .

II. Nitroalcohols containing C_5 .

β -Nitrodiethylcarbinol, $\text{NO}_2\cdot\text{CHMe}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Me}$, is formed by the addition of nitroethane to propaldehyde. It is a colourless liquid with a slight aldehydic odour, and is readily soluble in alcohol or ether. Its sp. gr. = 1.071 at 14° , and it boils at $118-121^{\circ}$ under 43 mm. pressure. *Methyl- α -nitropropylcarbinol*, obtained by the addition of nitropropane, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{NO}_2$, to acetaldehyde, distils at 112° under 36 mm. pressure. *Nitromethylisopropylcarbinol*, $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$, is obtained by the combination of nitro-

methane with isobutaldehyde. Its sp. gr. = 1.096 at 14°, and it distils at 120—123° under 40 mm. pressure. *β-Nitroisoamylic alcohol*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{NO}_2) \cdot \text{CHMe}_2$, boils at 138—139° under 36 mm. pressure, and its sp. gr. = 1.0966.

III. Nitro-alcohols containing C_6 .

Nitromethylisobutylcarbinol, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHMe}_2$, formed by the union of nitromethane with isovaleraldehyde, distils at 127—130° (38 mm.), and its sp. gr. = 1.025 at 14°. *Methyl-α-nitroisobutylcarbinol*, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}(\text{NO}_2) \cdot \text{CHMe}_2$, obtained from nitroisobutane and acetaldehyde, boils at 119—123° (38 mm.), and its sp. gr. = 1.0533.

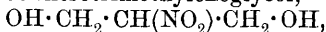
IV. Halogen derivatives of nitro-alcohols.

β-Chloronitropropylic alcohol, $\text{OH} \cdot \text{CH}_2 \cdot \text{CCl}(\text{NO}_2) \cdot \text{CH}_3$, obtained by the union of formaldehyde with chloronitroethane, is a colourless oil which solidifies on cooling to large, prismatic needles melting at 13.5°. Its sp. gr. = 1.37 at 14°, and it boils at 115° under 44 mm. pressure. The corresponding *ββ-bromonitropropylic alcohol*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CBr}(\text{NO}_2) \cdot \text{CH}_3$, melts at 42°. It has been found impossible to obtain iodonitroethane in a pure form. J. J. S.

Trimethylene Derivatives. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, 16, 213—217. Compare *Abstr.*, 1897, i, 1).—*Trimethylenic iodohydrin*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{I}$, obtained by the action of sodium iodide on a solution of the chlorhydrin in methylic alcohol, is a colourless, limpid liquid which turns brown on exposure to sunlight. It is only sparingly soluble in water, but dissolves readily in alcohol or ether. Its sp. gr. = 2.349 at 13°, and it boils at 115° under 38 mm. pressure, and at 225° under 758 mm. pressure without undergoing decomposition.

Trimethylenic iodacetate, $\text{OAc} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{I}$, may be obtained in a similar manner from the corresponding chlorine derivative. It is a colourless liquid with an agreeable odour, boiling at 207—210° under 757 mm. pressure, and at 112—115° under 38—40 mm. pressure. Its sp. gr. = 2.112 at 13°. J. J. S.

Nitro-Alcohols. By LOUIS HENRY (*Ber.*, 1897, 30, 2206—2207).—Attempts to prepare nitrotrimethyleneglycol,



by the partial condensation of nitromethane with formaldehyde proved unsuccessful, three molecules of the aldehyde taking part in the reaction, with formation of nitroisobutylglycerol (nitrotrihydroxyisobutane), $\text{NO}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{OH})_3$ (Piloty and Ruff, *Abstr.*, 1897, i, 453). When bromonitromethane is employed, however, *bromonitrotrimethyleneglycol*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CBr}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{OH}$, is formed in colourless crystals. The author hopes to convert this substance into glycerol by reduction, followed by substitution of hydroxyl for the amido-group.

A. H.

Glyceryl Monochlorhydrin from Allylic Alcohol. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, 16, 208—212).—Hanriot (*Bull. Soc. Chim.*, 29, 399) has cast some doubt on the constitution of the compound previously obtained by the author by the addition of hypochlorous acid to allylic alcohol. It is now pointed out that analogy and also the properties of the compound point to the constitution

previously given, namely, $\text{OH}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{OH}$. In similar cases of the addition of hypochlorous acid to propylene derivatives containing the grouping $-\text{CH}:\text{CH}_2$, it has been shown that the chlorine atom attaches itself to the CH -group and the hydroxyl radicle to the CH_2 -group. Further, when the monochlorhydrin is reduced with sodium amalgam and water, α -propylene glycol, $\text{CH}_2(\text{CH}_2\cdot\text{OH})_2$, is formed. When the chlorhydrin is oxidised with nitric acid, oxalic acid is the chief product. A better yield of the chlorhydrin is obtained if the crude product is extracted with alcohol and potassium carbonate instead of with ether as previously recommended.

J. J. S.

Constitution of Penterythritol. By GABRIEL GUSTAVSON and Miss O. POPPER (*J. pr. Chem.*, 1897, [ii], 56, 95—96).—When penterythritol tetrabromhydrin is repeatedly heated at 125° with alcoholic potash until all the bromine has been removed, *penterythritol ethylic ether*, $\text{C}(\text{CH}_2\cdot\text{OEt})_4$, is the sole product, which fact confirms Tollens' and Wigand's view of the constitution of penterythritol. The ether forms a syrup insoluble in water; it boils at 220 — 225° , and does not solidify at -18° ; it has sp. gr. = 0.9229 at $0^\circ/4^\circ$, 0.9082 at $16^\circ/4^\circ$, and 0.9017 at $21^\circ/4^\circ$; its index of refraction = 1.41647 at 21° ; hydriodic acid hydrolyses it to penterythritol and ethylic iodide.

C. F. B.

Isomaltose. By HERMANN OST (*Chem. Zeit.*, 1896, 20, 701—702).—In a former paper (*ibid.*, 1895, 19, 1501), the author brought forward experimental evidence showing that the so-called isomaltose of Lintner is merely impure maltose, and that the osazone obtained from it is identical with maltosazone (compare also *Trans.*, 1895, 702, 709, 739; 1897, 508). He, moreover, expressed his conviction that the synthetic hexabiose (glucobiose), obtained and named isomaltose by E. Fischer (*Abstr.*, 1891, 412), yielded an osazone consisting essentially of maltosazone; it therefore appeared that the synthesis of maltose had been effected. Fischer has, however, since refuted this view (*Abstr.*, 1896, i, 119).

The present paper recounts the author's more recent experiments. Dealing with Lintner's isomaltose, he states that when that portion of the products of starch hydrolysis which is soluble in 95 per cent. alcohol, consisting principally of maltose, is fermented with yeast, the residue does not give the osazone reaction (compare Brown and Morris, *Trans.*, 1895, 729; Ling and Baker, *ibid.*, 1897, 520).

The synthetic isomaltose is best prepared by the action of 33 per cent. sulphuric acid on glucose (and also on maltose) at the ordinary temperature for $4\frac{1}{2}$ months. After neutralisation, the filtered solution is brought to a concentration of 10—12 per cent. and sown with washed and pressed brewery yeast, amounting to half the weight of the glucose used, fermentation being allowed to proceed at 20 — 25° . On the following day, a fresh quantity of yeast equal in amount to the first is added. No further evolution of carbonic anhydride is observed at the end of 2 days, but the liquid is placed in an incubator at 30° for 3 days. The unfermented residue represents 27 per cent. of the glucose employed, and consists essentially of isomaltose. This iso-

maltose has up to the present only been obtained as a syrup; its specific rotatory power may probably be placed at about $[\alpha]_D = +70^\circ$ and its cupric reducing power (by Sachsse's method) at 58—65 per cent. that of maltose. The osazone was found to have the composition of a hexabiosazone, and after being dried at 100° , it melted at 130 — 145° ; its optical rotatory power in alcoholic solution examined with Auer light was " $[\alpha]_{\text{Auer}}$ " = -15° to -20° . A. R. L.

Analytical Investigation of the Hydrolysis of Starch by Acids. By GEORGE W. ROLFE and GEORGE DEFREN (*J. Amer. Chem. Soc.*, 1896, 18, 869—900; 1897, 19, 261—263).—The authors' experiments were carried out in a modified autoclave from which quantities of the solution undergoing hydrolysis could be removed at any desired moment. As a rule, about 100 grams of starch were mixed with a litre of water, containing hydrochloric acid, the maximum concentration of the latter being a N/10 solution and the minimum a N/1000 solution. Sulphuric acid and oxalic acid were also used. Samples of 50—75 c.c. of the solution were removed at different stages of the hydrolysis, shaken with an excess of marble dust, and two drops of N/10 sodium hydroxide added. The specific gravity, total solids (by 3.86 divisor), specific rotatory power, and cupric reducing power were then determined in the clear filtrate.

The authors have incidentally determined the relation between angular degrees for sodium light, as furnished by polarimeters of the Laurent type, and divisions of the Ventzke scale, furnished by instruments employing ordinary light and quartz compensation, and find, with standard quartz plates, the usual factor, namely, 0.346, whilst with solutions of glucose they obtained the factor 0.344, which is in agreement with Rimbach's results (*Abstr.*, 1894, ii, 486. Compare Brown, Morris, and Millar, *Trans.*, 1897, 93).

The results point to the fact that the cupric-reducing power of the total product bears a constant relation to the specific rotatory power, even when starch is hydrolysed under widely varying conditions. Hence, given the one, the value of the other can be calculated. To a rotation of about 90° , the plotted results coincide extremely closely with the arc of a circle, the equation of which is $x^2 + y^2 - 758x + 772.4y = 0$, which exactly intercepts the "zero" and "hundred" points at $[\alpha]_D = 195^\circ$ and 53.5° respectively. The curves obtained by plotting the percentages of maltose, dextrin, and glucose as ordinates, and the specific rotatory powers as abscissæ in the same ordinate system are quite as noteworthy.

The dextrin curve gradually falls from 100 per cent. to zero near the rotation corresponding with that of glucose, namely, $[\alpha]_D = 53.5^\circ$, whilst the maltose curve reaches a maximum percentage of 44.1 at about $[\alpha]_D = 129^\circ$, corresponding with the usual state of conversion of commercial glucose and then falls, disappearing at $[\alpha]_D = 53.5^\circ$. The glucose curve steadily mounts to 100 per cent. At the point where the maximum percentage of maltose is present, the glucose and dextrin are present in equal quantity, as shown by the intersection of the curves. The authors have calculated a table from the curves, which gives the values of maltose, glucose, and dextrin within one-

tenth per cent. for successive stages of acid hydrolysis represented by each degree of rotation between $[\alpha]_D = 195^\circ$ and 53.5° .

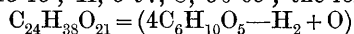
With the data at hand, the authors sought to determine whether a sample of commercial glucose is a product of one hydrolysis or a mixture of two separate ones. Since in a factory the time occupied in filling a converter is about one-third of the total time required for the hydrolysis, there must be a great difference in the time of hydrolysis of different portions of the starch. Despite this, however, the authors find that samples made in one operation conform to their table, and there appears to be strong evidence that those which depart from it are mechanical mixtures. The authors draw the following conclusions from their results. That in any homogeneous acid-converted starch-product the specific rotatory power corresponds with a definite chemical composition. That but three simple carbohydrates (leaving reversion products out of consideration), possibly in molecular aggregates, exist in a solution of a starch product hydrolysed by acids.

The usual practice in glucose factories of determining the degree of conversion of the starch is by means of the iodine reaction; the tint at which the conversion is considered complete coincides with a solution of the conversion products having a specific rotatory power between the limits of the rotations $[\alpha]_D = 128^\circ$ and 135° . A. R. L.

Soluble Starch. By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1897, 30, 2108—2110).—It is shown that "soluble starch" is quite different from "amylodextrin," since the former gives a pure blue coloration with iodine, and does not reduce Fehling's solution, whilst the latter gives a reddish-brown coloration with iodine and slowly reduces Fehling's solution. Soluble starch is best prepared by treating rice starch with a small quantity of a 1 per cent. solution of potassium hydroxide, leaving it for some time, then adding excess of the alkali, and heating on the water bath with repeated shaking for from 20—30 minutes; the product is then filtered, rendered slightly acid with acetic acid, and precipitated by the addition of alcohol. It can be purified by repeated dissolution in water and precipitation with alcohol; the snow-white product prepared in this way contains very little ash, and is soluble in water to the extent of about 4 per cent.

J. F. T.

Oxycellulose. By LÉO VIGNON (*Compt. rend.*, 1897, 125, 448—450).—Oxycellulose is best prepared by the action of potassium chlorate and hydrochloric acid on carefully purified cotton wool. 150 grams of the chlorate is dissolved in 3 litres of water, 30 grams of purified cotton is added, and 125 c.c. of hydrochloric acid of 22° gradually stirred in. The liquid is heated nearly to boiling for about an hour, and the product is washed with water, and finally with alcohol; 87.58 per cent. of the oxycellulose thus prepared dissolves in fused potash at 180° , whereas only 12.0 per cent. of cellulose dissolves. It would follow that the product is a mixture of 75 per cent. of oxycellulose with 25 per cent. of cellulose. On this basis, the composition of the oxycellulose is C, 43.15; H, 5.97, O, 50.65; the formula



requires C, 43.5; H, 5.7; O, 50.7.

The heats of combustion are, cellulose 4190 to 4224, oxycellulose 4124 to 4133; the heat developed by immersion in normal potassium hydroxide solution is, cellulose 0.74, oxycellulose 1.30 Cal. per 100 grams, and hence the energy of the acidic function has increased. The power of absorbing colouring matters such as safranin or methylene blue has also greatly increased.

Oxycellulose dissolves in aqueous potash, yielding a golden-yellow solution, which reduces Fehling's solution; it gives a white precipitate when acidified with hydrochloric acid. The oxycellulose itself energetically reduces Fehling's solution, but the residue left after extracting with hot potassium hydroxide solution has lost this reducing power. With Schiff's reagent, oxycellulose gives an intense violet coloration, and therefore has an aldehydic function. C. H. B.

Aliphatic Nitramines. By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1897, 16, 226—228. Compare Bamberger, *Abstr.*, 1897, i, 468).—A mixture of methylnitramine with potassium nitrite in molecular proportion reacts in aqueous solution, yielding nitrogen, potassium nitrate, methylic alcohol, and the two isomeric dimethylnitramines. Small quantities of carbonic anhydride and of an extremely volatile oil with an isonitrilic odour are obtained as bye-products. The author considers that this decomposition is best represented by supposing an additive compound, $\text{NO}_2 \cdot \text{NMe} \cdot \text{N}(\text{OH})_2$, to be first formed by the union of the nitrous acid with methylnitramine. It follows that methylnitramine is capable of oxidising nitrous to nitric acid.

The author also finds that colours similar to that mentioned by Bamberger as being produced by the action of zinc dust and acetic acid on a solution of benzenediazoic acid and α -naphthylamine are also produced by aliphatic nitramines when their acetic acid solutions are mixed with zinc and α -naphthylamine, aniline, dimethylaniline, or phenylenediamine. J. J. S.

Cystin. By CAMILLE CHABRIÉ (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 72—73).—Külz showed that cystin may originate during the pancreatic digestion of proteids, and this suggested that it may be formed by the action of hydrogen sulphide on amido-acids. In carrying out the investigation, the gas was passed through a mixture of aldehyde-ammonia with ether, and a crystalline substance, soluble in ether and melting at 60—63°, was obtained of the constitution



The appearance of this new substance is held to be confirmatory of the hypothesis stated above concerning the origin of cystin.

W. D. H.

Volatilisation of Lactic Acid and its Anhydrides at the Ordinary Temperature; Volatilisation of Lactic Acid with Water Vapour. By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1896, [iii], 15, 1206—1210).—When solutions of lactic acid are evaporated to dryness in a vacuum over sulphuric acid, and then kept in a vacuum over solid potash, part of the acid is converted into anhydride, and part volatilises, the loss in four days amounting to 0.0112 gram, and in 11 days to 0.0217 on an original quantity of 0.1280 gram. Similar results were obtained with ethereal solutions of the acid. The rate

of evaporation is lower the higher the proportion of lactic anhydride present; the anhydride itself is practically non-volatile in a vacuum at the ordinary temperature. Lactide, on the other hand, is distinctly volatile; 0.1406 gram lost 0.0046 gram in 13 days, and 0.0246 gram in 49 days.

Boiling solutions of lactic acid lose only a small quantity of the acid, and the loss is directly proportional to the quantity of acid in the solution. The loss of lactic acid when more or less concentrated solutions are exposed to dry air or in a dry vacuum is not due to mechanical removal with the water vapour, but must be attributed to the volatility of the acid itself. This volatility introduces noteworthy errors into the estimation of lactic acid in wines when the latter are evaporated to dryness. (Compare this vol., ii, 57.)

C. H. B.

Formation of Chains. XIV. Aniline and Ethylic Salts of Fatty Brominated Acids. By CARL A. BISCHOFF (*Ber.*, 1897, 30, 2303—2310).—This investigation was carried out with the object of determining whether the conditions which regulate the formation of carbon chains were applicable to the formation of carbon-nitrogen chains, and it was found, as far as the investigation was carried, that double alkyl groups, such as isopropyl, isoamyl, &c., have precisely the same effect in the latter case as in the former. During the course of the investigation, *ethylic α -anilidobutyrate*, which had previously only been obtained as an oil, was isolated as a colourless, crystalline substance melting at 29°.

J. F. T.

Formation of Chains. XV. Aniline and Fatty Brominated Acid Amides.—Bromacetamide reacts more readily with aniline than the chlorinated derivative, the reaction taking place at a much lower temperature, and if this be not allowed to exceed 130°, *phenylimidodiacetamide*, $\text{NPh}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, is obtained in nodular masses melting at 225°; if, however, the reaction be carried out at 170°, *phenylimidodiacetamide* melting at 159° is formed. *α -Bromopropionamide*, $\text{CHBrMe} \cdot \text{CO} \cdot \text{NH}_2$, prepared in an analogous manner to bromacetamide, crystallises from benzene in slender leaflets melting at 123°, and on condensation with aniline at 98° yields *α -anilidopropionamide* and at 180° *α -anilidopropionanilide*. *α -Bromobutyramide*, $\text{CHBrEt} \cdot \text{CO} \cdot \text{NH}_2$ crystallises from acetone in needles melting at 112°, and yields *α -anilidobutyramide* on condensation with aniline, the corresponding anilide being formed in small quantity only. *α -Bromoisobutyramide*, $\text{CBr} \cdot \text{Me}_2 \cdot \text{CO} \cdot \text{NH}_2$, melting at 148°, condenses with aniline with the formation of an *anilidoisobutyramide* melting at 136°; this, however, is the β -derivative, and identical with the compound obtained by Tiemann from anilidoisobutyronitrile.

J. F. T.

Formation of Chains. XVI. Formation of Acid Anilides. By CARL A. BISCHOFF (*Ber.*, 1897, 30, 2315—2322).—After it had been shown (compare preceding abstracts) that the formation of anilides from anilido-fatty acids according to the equation

$$2\text{NH}_2\text{Ph} + \text{CBr}(a)(b) \cdot \text{CO} \cdot \text{NH}_2 = \text{NHPh} \cdot \text{C}(a)(b) \cdot \text{O} \cdot \text{NHPh} + \text{NH}_4\text{Br},$$

only occurred when $a = \text{CH}_3$ and $b = \text{H}$, and not when $a = \text{C}_2\text{H}_5$, or a and $b = \text{CH}_3$, similar experiments were tried with the α -bromo-fatty

amides and aniline, and it was found that the general result was the same. J. F. T.

Preparation of Diethyl Malonate. By WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1896, 18, 1105—1106).—The preparation of diethyl malonate is very much shortened if sulphuric acid is used instead of hydrochloric, and sodium hydrogen carbonate instead of potassium carbonate. Sodium hydrogen carbonate (90 grams) is added to a warm solution of chloracetic acid (100 grams) in water (200 c.c.), and the heating continued until the temperature is 55—60° and effervescence has nearly ceased; coarsely powdered potassium cyanide (80 grams) is then added, the whole kept well stirred, and the solution quickly evaporated until the temperature reaches 130—135°. When cold, the mass is broken up and transferred to a litre flask containing 40 c.c. of alcohol and connected with a reflux condenser. A well cooled mixture of 160 c.c. of alcohol and 160 c.c. of concentrated sulphuric acid is slowly added, the operation taking 5—10 minutes instead of 1—1½ days as in the old method, and the action is completed on the water bath. The mixture is cooled, well shaken, and water (200 c.c.) added; the undissolved crystals are collected and well washed with ether, the ethereal washings being used for extracting the filtrate. The ethereal solution after being washed with excess of sodium carbonate solution is distilled, when it yields nearly pure ethyl malonate. J. J. S.

Action of Acid Anhydrides on Acids and their Salts. Formation of Ketodilactones, Ketonic Acids and Ketones. By RUDOLPH FITTIG (*Ber.*, 1897, 30, 2145—2150).—When tricarballic acid is heated with acetic anhydride, a compound of the formula $C_7H_8O_4$ is obtained, which is readily soluble in chloroform, melts at 98° and is neutral, but when boiled with bases yields salts of the dibasic acid, $C_7H_{10}O_5$. This neutral substance appears to be identical with the ketodilactone, $CO \begin{array}{c} \diagup O-CH_2 \\ \diagdown CH-CH_2 \end{array} \cdot O \cdot CO$, described

by Emery (*Abstr.*, 1897, i, 325). It seems to be formed by the direct displacement of the hydrogen atom of the CH group in tricarballic acid by the acid radicle, carbonic anhydride and water being subsequently eliminated. Thus, butyric anhydride produces an analogous compound, $C_9H_{12}O_4$, which melts at 55°; benzoic anhydride reacts in a similar manner, and the compound formed melts at 137°. The production of this substance shows that the reaction proceeds in the manner indicated above, and not by the formation of a mixed anhydride of tricarballic acid, from which the ketodilactone might result by loss of water and carbonic anhydride. When tricarballic acid, in the form of the sodium salt, is heated with acetic anhydride and benzaldehyde, the *benzylidene* derivative of the ketodilactone, $C_7H_6O_4 \cdot CHPh$, is formed, which crystallises in lustrous plates melting at 160°. In the presence of valeraldehyde or heptaldehyde, on the other hand, the compound $C_7H_8O_4$ is formed.

This direct substitution of an acid radicle for hydrogen is not limited to tricarballic acid, for acetic anhydride and other anhydrides act in a similar manner with various other acids. Thus, acetic

anhydride reacts very violently with sodium succinate at 130°, the whole mass becoming carbonised, whilst both in this case and when the free acid is employed, a small amount of levulinic acid is produced. A similar violent action occurs between acetic anhydride and sodium itaconate.

It seems probable that the production of hydrochelidonic acid, from succinic anhydride, and the formation of ketones by the action of phosphoric anhydride on the fatty acids, and by the action of acetic anhydride on the fatty acids and their salts, may be brought about in a similar manner. Further investigations are being made into the course of the reaction.

A. H.

Rupture of the Carbon Chain in Ethylic Dicarboxyglutaconate (Ethylic $\omega_2\omega_2'$ -Propenetetracarboxylate). By MAX GUTHZEIT and HERBERT W. BOLAM (*J. pr. Chem.*, 1896, [ii], 54, 359—376).—Alkaline hydrolysing agents act on ethylic dicarboxyglutaconate quite differently from acids; on hydrolysis with alkaline hydroxides, this ethylic salt is partially split up into malonic and formic acids, whereas no rupture of the chain takes place when it is treated with acids.

With barium hydroxide, using a 10 per cent. solution, 25 per cent. of the salt is decomposed, and with a 20 per cent. solution 50 per cent. With potassium hydroxide, when 3 mols. of the hydroxide are used, and the hydrolysis conducted at the boiling point of the solution, 30 per cent. of the ethylic salt is decomposed, although a 20 per cent. solution of the hydroxide allowed to remain in contact with the ethylic salt at the ordinary temperature for some weeks does not cause any rupture of the chain.

Barium hydroxide (25 per cent. solution) hydrolyses ethylic benzyl-dicarboxyglutaconate even at 100°, almost quantitatively to benzylglutaconic acid, only a small quantity of malonic acid being formed.

When treated with acids, ethylic dicarboxyglutaconate is hydrolysed without any decomposition of the acid taking place. Hydrochloric acid gives the best result, 50—60 per cent. of the theoretical yield of dicarboxyglutaric acid being obtained by this means.

J. F. T.

Thioureas. By ERNST A. SCHMIDT (*Arch. Pharm.*, 1897, 235, 435—441).—Bromo- and iodo-thiosinamine have been shown to be derivatives of ψ -propylenethiourea which has been obtained by Gabriel from thiosinamine by intramolecular change. The physiological action of these three compounds is very similar, and hence confirms this relationship of chemical constitution. The halogen derivatives are, in spite of their much higher molecular weight, a little more active than ψ -propylenethiourea itself.

The three isomeric substances thiosinamine, ψ -propylenethiourea, and trimethylenethiourea differ distinctly in their physiological effects.

E. W. W.

Ethylenethiourea and Trimethylenethiourea. By WALTER SCHACHT (*Arch. Pharm.*, 1897, 235, 441—468).—Ethylenethiourea prepared by Hofmann's method (this Journal, 1872, 501), melts at 194° according to the author. By mixing aqueous solutions of this sub-

stance and of mercuric chloride, a double compound, $2C_3H_6N_2S, 3HgCl_2$, is formed. Compounds of the following composition were also prepared in a similar way: $(C_3H_6N_2S)_3, AgCl$, $(C_3H_6N_2S)_2, PtCl_4$, $(C_3H_6N_2S)_2, Cu_2Cl_2$, $(C_3H_6N_2S)_2, Hg(CN)_2$. Ethylenethiourea also unites with silver nitrate and with gold chloride to form compounds $C_3H_6N_2S, AgNO_3$ and $(C_3H_6N_2S)_2, AuCl$; both these, when treated with picric acid, yield compounds having the formula $C_3H_5N_2S, Ag, C_6H_2(NO_2)_3OH$ and $(C_3H_6N_2S)_2, AuOC_6H_2(NO_2)_3$ respectively. By triturating ethylenethiourea with mercury, or with finely divided silver or copper, in the presence of alcohol, the alcoholic extract, after separation of the unchanged ethylenethiourea, does not crystallise but contains the metal, and yields a flocculent precipitate with picric acid. The compound with methylic iodide, $C_3H_6N_2S, MeI$, crystallises in transparent, hexagonal prisms, easily soluble in water and chloroform, and melting at 145° ; the corresponding methochloride obtained by treating the iodide with silver chloride, forms rhombic crystals and melts at 92° . Its *platinochloride*, $(C_3H_5N_2S, MeCl)_2, PtCl_4$, crystallises in small, red crystals and melts at 178° ; the *aurochloride* in yellow needles melting at 194° , and the picrate in yellow needles melting at 180° . The *ethiodide* is less stable and more hygroscopic, melts at about 157° , the corresponding *platinochloride* at 174° , and the *aurochloride* at 142° .

From the methochloride, the free base was obtained as a viscid alkaline liquid by the action of sodium hydroxide; the *aurochloride* prepared from this melted at 194° , and was identical with the *aurochloride* obtained from the product of the action of methylic iodide on ethylenethiourea silver nitrate by means of silver chloride. In the metallic salts and the halogen compounds, therefore, the metal and the alkyl group are assumed to be directly united to sulphur by displacement of the hydrogen of the SH group. In ethylenethiourea this acid group is supposed to counterbalance the basic character of the nitrogen groups, whereas when the hydrogen of this group has undergone substitution, the basic character is developed, and salts with picric acid may be prepared.

The ethylenic bromide compound, $(C_3H_6N_2S)_2, C_2H_4Br_2$, which crystallises in brown, transparent needles, decomposes without melting, and yields an *aurochloride*, a *platinochloride* and a picrate which are not crystalline. The corresponding chlorine compound was prepared from the bromide, and its *platinochloride* and *aurochloride* obtained as amorphous precipitates. By the action of concentrated fuming hydrochloric acid or concentrated sulphuric acid at 150° , ethylenethiourea is decomposed with liberation of hydrogen sulphide and sulphur and formation of ethylenediamine hydrochloride. Trimethylenethiourea forms double compounds which are very similar to those of ethylenethiourea, and with mercury, silver, and copper it undergoes a similar reaction. Fuming hydrochloric acid and sulphuric acid effect decomposition with greater difficulty than in the case of ethylenethiourea.

E. W. W.

Ketopentamethylene from Vinyltrimethylene Bromide. By GABRIEL GUSTAVSON and Miss H. BULATOFF (*J. pr. Chem.*, 1897, [ii],

56, 93—95).—The ketone which is formed, together with an aldehyde, when vinyltrimethylenic bromide (Abstr., 1896, i, 669) is heated with lead oxide and 10—15 parts of water for 6 hours at 135—140°, has been identified as ketopentamethylene, C_5H_8O . No doubt the aldehyde is first formed, and then undergoes a transformation into the ketone; this transformation of a trimethylene into a pentamethylene derivative is noteworthy. The formation and reactions of "vinyltrimethylene" can be equally well, perhaps better, explained by regarding it as methylenetetramethylene, $CH_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} C:CH_2$. C. F. B.

Electrolytic Reduction of Nitrobenzene. By WALTHER LÖB (*Zeit. Elektrochem.*, 1897, 3, 471—474).—The experiments were undertaken in the hope of obtaining amidobenzoic acids in analogy with Gattermann's preparation of amidophenols by electrolytic reduction of nitro-compounds in sulphuric acid solution, or with the author's synthesis of chlorinated or brominated anilines by reduction of the nitrobenzenes in solutions containing hydrochloric or hydrobromic acids (Abstr., 1896, i, 605). A solution of nitrobenzene in 4 parts of formic acid to which a few cubic centimetres of strong sulphuric acid are added, in order to increase the conductivity, surrounds the lead or platinum cathode; the carbon or platinum anode is immersed in dilute sulphuric acid, and the two liquids are separated by a porous partition, the apparatus used being that previously described (Abstr., 1897, i, 331). The reduction is at an end when hydrogen begins to escape. The principal product of the reaction was benzidine formate, 70 per cent. of the theoretical yield being obtained; azobenzene, aniline, and a violet-blue base were also isolated in small quantities. The results were not influenced by the temperature, current density or concentration within the fairly wide limits employed. In acetic acid solution, benzidine is again the principal product, azobenzene and traces of paramidophenol being also formed; the addition of oxalic acid to the acetic acid solution makes practically no difference. In ammoniacal solution containing 10 grams of nitrobenzene, 70 c.c. of alcohol, 30 c.c. of strong aqueous ammonia, and 5 grams of ammonium chloride, the products of the electrolytic action were different, 2 grams of hydrazobenzene and 5.5 grams of azobenzene being obtained. T. E.

Phosphates from the Phenols. By WILHELM AUTENRIETH (*Ber.*, 1897, 30, 2369—2381).—Phosphorus oxychloride readily reacts with phenols in presence of aqueous soda to form two series of compounds, the normal phosphates, $PO(OR)_3$, and the diphosphates $PO(OR)_2 \cdot OH$. The latter are also produced by the hydrolysis of the normal phosphates, and may be converted into chlorides and amides. They are very stable towards acids and alkalis, and many of them are precipitated from aqueous solution by dilute hydrochloric acid. When phenol is treated with phosphorus oxychloride in this manner, triphenylic phosphate and diphenylphosphoric acid [diphenylic hydrogen phosphate] are produced. The latter, when pure, crystallises well, is moderately soluble in water, and melts at 61—62° (compare Rapp, Abstr., 1884, 1337). *Triparatolylic phosphate*, $PO(O \cdot C_6H_4Me)_3$, crystallises in white needles

melting at 77—78°. *Diparatolylic phosphate*, $\text{PO}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_2\cdot\text{OH}$, yields an *amide* which crystallises in nacreous plates melting at 146°, and is almost insoluble in water. *Triparachlorophenylic phosphate* crystallises in lustrous, slender needles melting at 99—100°. *Diparachlorophenylic phosphate* forms lustrous, colourless plates and needles melting at 126—127°; the *sodium* salt crystallises in nacreous plates; whilst the *chloride* forms slender needles, and the *amide* lustrous plates melting at 152°. *Tri-β-naphthylic phosphate*, has been previously described by Heim (Abstr., 1883, 1108). *Di-β-naphthylic phosphate*, $\text{PO}(\text{O}\cdot\text{C}_{10}\text{H}_7)_2\cdot\text{OH}$, crystallises in prisms melting at 147—148°; the *sodium* salt forms lustrous plates. The acid is only sparingly soluble in water and is precipitated from aqueous solution by dilute hydrochloric acid; the *amide* crystallises in lustrous plates, melting at 215°. *Tri-1-chloro-2-naphthylic phosphate* crystallises in slender, white needles, melting at 152°. *Di-1-chloro-2-naphthylic phosphate*, $\text{PO}(\text{O}\cdot\text{C}_{10}\text{H}_6\text{Cl})_2\cdot\text{OH}$, forms slender needles and melts at 251°. *Tri-α-naphthylic phosphate* crystallises in lustrous needles melting at 145°.

A comparison of the melting points of the various substances described shows that the normal ethers melt at a lower temperature than the diphosphates and these again at a lower temperature than their amides.

A. H.

Nitrosoderivatives of Phloroglucinol Diethyl Ether. By HUGO WEIDEL and J. POLLAK (*Monatsh.*, 1897, 18, 347—378. Compare Abstr., 1897, i, 42).—By the action of potassium nitrite and acetic acid on the diethyl ether of phloroglucinol, Moldauer obtained two isomeric mononitroso-derivatives, which he called *α*- and *β*-diethoxyquinone-oximes. He was, however, unable to determine either the position of the nitroso-group or whether the derivatives were true nitroso- or isonitroso-compounds.

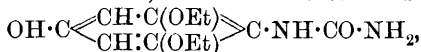
The authors find that the two diethoxyquinoneoximes give different products on reduction, and these reduction products give different acetyl derivatives, thus proving Moldauer's statement that the two diethoxyquinoneoximes cannot be stereoisomerides.

With regard to the position of the amido-group in the products of reduction, either it must lie between an ethoxy- and a hydroxyl group or between two ethoxy-groups, thus, $\text{OH}\cdot\text{C}\begin{smallmatrix} \swarrow \text{C}(\text{NH}_2) \cdot \text{C}(\text{OEt}) \\ \searrow \text{CH}=\text{C}(\text{OEt}) \end{smallmatrix} \gg \text{CH}$ or

$\text{OH}\cdot\text{C}\begin{smallmatrix} \swarrow \text{CH} \cdot \text{C}(\text{OEt}) \\ \searrow \text{CH} \cdot \text{C}(\text{OEt}) \end{smallmatrix} \gg \text{C}\cdot\text{NH}_2$. This point could not be settled by the

action of acetic anhydride, which gave only triacetyl derivatives, but by the action of carbamide on the hydrochlorides of the two reduction products, 3:5-diethoxycarbonyl-2-amidophenol, $\text{CO}\begin{smallmatrix} \swarrow \text{NH} \cdot \text{C} \cdot \text{C}(\text{OEt}) \\ \searrow \text{O}-\text{C}-\text{CH} \end{smallmatrix} \text{CH}$

was produced in the one case, and a substituted carbamide,



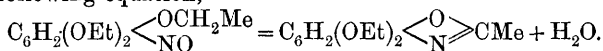
in the other, thus definitely proving the position of the amido-group in the products of reduction, and consequently the position of the nitroso-groups in the phloroglucinol derivatives.

Moldauer showed that both nitroso-derivatives can be further

ethylated, α -diethoxyquinoneoxime with production of ethyl pyriphlorone diethyl ether and a red triethyl ether, whereas β -diethoxyquinoneoxime yields only a triethyl ether. By reduction of these triethoxy-compounds, the authors show that both contain, combined directly to nitrogen, an ethoxy-group which can be eliminated as alcohol; they must therefore be regarded as oxime ethers, and the original substances as isonitroso-derivatives: and Moldauer's α - and β -diethoxyquinoneoximes are respectively 3:5-diethoxyorthoquinone-2-monoxime and 3:5-diethoxy-paraquinone-4-monoxime.

When ethyl pyriphlorone diethyl ether is treated with reducing agents, the elements of water attach themselves, and the product, the monacetyl derivative of 3:5-diethoxy-2-amidophenol, when heated with sulphuric acid, loses acetic acid, and with acetic anhydride, gives a substance identical with the triacetyl derivative of 3:5-diethoxyorthoamidophenol. Further, on reducing pyriphlorone with tin and hydrochloric acid, the hydrochloride of 3:5-diethoxy-2-amidophenol is obtained. These experiments, together with the fact that the monacetyl derivative of 3:5-diethoxy-2-amidophenol, on distillation, loses water with formation of pyriphlorone, shows the latter to be 3:5-diethoxyethenyl-2-amidophenol.

The unusual formation of an ethenyl derivative from an oxime by the action of alcoholic potash and ethylic iodide, may be explained by supposing that reduction takes place, a part of the alcohol being oxidised to acetic acid, which unites with the intermediate product of reduction, forming 3:5-diethoxyethenyl-2-amidophenol; or 3:5-diethoxyorthoquinoneoxime acts partially as a true nitroso-compound, giving a triethyl ether in which the third ethoxy-group is connected to carbon. Such an ether could be converted into an ethenyl derivative according to the following equation,



Certain modifications for the preparation of phloroglucinol diethyl ether are given, by which means almost a quantitative yield of the ether can be obtained and also the bye-products, namely diresorcinol, and the monethyl ether of phloroglucinol, can be isolated.

Phloroglucinol monethyl ether crystallises from benzene in large, colourless, needle-shaped crystals melting at 72—73° (uncorr.). When crystallised from water, it contains 2H₂O.

2-Amido-3:5-diethoxyphenol hydrochloride, obtained by reducing 3:5-diethoxyorthoquinone-2-monoxime, crystallises from dilute hydrochloric acid in glistening needles, which become rose-red and then brown on exposure to the air. When heated to 130°, it decomposes without melting. The free amidophenol could not be obtained on account of the ease with which it decomposes in air. When the hydrochloride is treated with acetic anhydride, a *triacetyl* derivative is obtained, crystallising from light petroleum in needles and melting at 110°—112°. The *monacetyl* derivative crystallises in silken needles melting at 122.5—123.5° (uncorr.).

4-Amido-3:5-diethoxyphenol hydrochloride, obtained by reducing the corresponding paraquinoneoxime, crystallises in long, colourless, glistening monoclinic needles, which decompose at about 140° without melting.

The crystals, using water as a solvent, contain $1\text{H}_2\text{O}$. The *triacetyl* derivative separates from light petroleum in colourless, glistening needles melting at $81^\circ\text{--}83^\circ$ (uncorr.).

3 : 5-Diethoxycarbonyl-2-amidophenol, prepared by heating carbamide with 2-amido-3 : 5-diethoxyphenol, crystallises from light petroleum in glistening needles which are almost insoluble in water, but readily soluble in boiling alcohol, benzene and ethylic acetate. It melts at $192\text{--}195^\circ$ and can be heated to 250° without undergoing decomposition.

2 : 6-Diethoxy-4-hydroxyphenylcarbamide, obtained by the action of carbamide on 4-amido-3 : 5-diethoxyphenol, separates from water acidified with acetic acid in small, glistening, prismatic needles, becoming yellow on drying and melting at $199\cdot5\text{--}201^\circ$ (uncorr.). A. W. C.

Metol [Paramethylamidophenol Sulphate]. By LUDWIG PAUL (*Zeit. angew. Chem.*, 1897, 171—174).—The photographic developer known as “metol” is shown by the author to be *paramethylamidophenol sulphate*, $[(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}]_2\cdot\text{H}_2\text{SO}_4$. The base, which crystallises from benzene in needles melting at 85° , when treated with nitrous acid, yields a *nitroso*-derivative crystallising in thick prisms, and when oxidised with lead peroxide yields quinone. The author has not been able to obtain the base by the direct methylation of paramidophenol, but has obtained it by heating parahydroxyglycocine at about 220° . J. J. S.

2 : 5-Diamidoquinone. By FRIEDRICH KEHRMANN and G. BETSCH (*Ber.*, 1897, 30, 2096—2103).—The preparation of 1 : 4-diamidoquinone was carried out in the following way : 2-amido-5-nitrophenol, prepared from paranitrodiazobenzeneimide, was reduced by means of tin and hydrochloric acid to hydroxyparaphenylenediamine, and this, by boiling with acetic anhydride and sodium acetate, was converted into *triacetylparaphenylenediamine*, $\text{C}_6\text{H}_3\text{Ac}(\text{NHAc})_2$, a substance crystallising from hot water in glistening plates melting at 234° . On treatment with dilute sodium hydroxide solution, this yields *diaceto-hydroxyparaphenylenediamide*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NHAc})_2$ [$\text{OH}:(\text{NHAc})_2 = 1 : 2 : 5$], an unstable compound crystallising from hot water in needles melting at 265° ; when oxidised with sodium dichromate in acetic acid solution, it gives 2 : 5-diacetamidquinone, $\text{C}_6\text{H}_2\text{O}_2(\text{NHAc})_2$ [$\text{O}_2:(\text{NHAc})_2 = 1 : 4 : 2 : 5$]. The latter crystallises from glacial acetic acid in straw-coloured needles partly subliming at 300° , and on hydrolysis with sulphuric acid yields 2 : 5-diamidoquinone [$\text{O}_2:(\text{NH}_2)_2 = 1 : 4 : 2 : 5$], a violet, crystalline powder melting at $325\text{--}330^\circ$. On reduction, 2 : 5-diacetamidquinone yields 2 : 5-diacetamidquinol, $\text{C}_6\text{H}_3(\text{OH})_2(\text{NHAc})_2$, which is a powder melting at $285\text{--}290^\circ$; 2 : 5-diamidoquinol itself is a white, unstable, crystalline compound, the hydrochloride of which is, however, stable in concentrated hydrochloric acid solution. The *tetracetyl* compound crystallises from glacial acetic acid in glistening needles melting at 190° . That the compound formed by the action of hydroxylamine on dihydroxyquinone does not possess the quinone formula as stated by Nietzki and Schmidt, is shown by its conversion into *sym*-diamidoresorcinol, which, on oxidation, gives amidohydroxyquinoneimide, and on acetylation a *tetracetyl*

compound crystallising from glacial acetic acid in needles melting at 180° , and identical with the compound derived from the diamidoresorcinol obtained from dinitroresorcinol.

J. F. T.

Diazotisation of Highly Substituted Anilines, and Formation of the Corresponding Benzonitriles. By ADOLPH CLAUS and REINHOLD WALLBAUM (*J. pr. Chem.*, 1897, [ii], **56**, 48—70).—Derivatives of aniline containing several negative groups cannot be diazotised in the usual way. They can be diazotised in large part, however, by dissolving them in sulphuric acid monohydrate, cooling the solution to -10 to -15° , and adding drop by drop a very concentrated aqueous solution of sodium nitrite (in considerable excess of the theoretical amount), the liquid being stirred vigorously by a mechanical stirrer during the addition, which should last $1-1\frac{1}{2}$ hours; on diluting the solution, the unaltered amine is often precipitated, and can be removed by filtration. Fuming 40 per cent. hydrochloric acid can sometimes be used instead of sulphuric acid. Many of these diazo-solutions react but little, or very imperfectly, with sodium naphthol-sulphonate to form azo-dyes; yet, even when they give no other of the ordinary diazo-reactions, they are found to yield cyanides by Sandmeyer's reaction. These cyanides, containing several negative groups, it has not yet been found possible to hydrolyse to the corresponding benzoic acid derivatives. In conclusion, it is pointed out that these highly substituted diazo-compounds do not appear to form sulphites, but yield sulphonates immediately; one of the authors (Claus) reiterates his opinion that diazo-sulphites and sulphonates are structurally, and not merely stereochemically, isomeric.

2:3:4:6-Tetrabromobenzonitrile was prepared from the corresponding tetrabromaniline, by the diazo-reaction; but it melts at 123° ; but after sublimation, at 102° . 2:3:4:5-Tetrabromaniline was prepared by nitrating the acetyl derivative of 3-bromaniline; then treating the mixture of 4- and 6-nitro-derivatives with bromine (2 mols.) in acetic acid solution; diazotising the mixture of 2:3:6-tribromo-4-nitro- and 2:3:4-tribromo 6-nitro-aniline, and displacing the diazo-group by bromine, by which means a single product, 1:2:3:4-tetrabromo-6-nitrobenzene, melting at 107° , was obtained, finally reducing the last-named substance with stannous chloride. It melts at 122° ; the 2:3:4:5-benzonitrile obtained from it at 124° . 2:3:6-Tribromo-4-nitraniline (see above) is yellow, and melts at 131° . 1:2:4-Tribromo 6-nitrobenzene can be obtained by the diazo-reaction from 2:4-dibromo-6-nitraniline; it melts at 81° (not 119° , Körner), and, when reduced with stannous chloride, yields 2:3:5-tribromaniline, melting at 91° . 2:6-Dibromo-4-nitraniline yields 1:2:6-tribromo-4-nitrobenzene by the diazo-reaction. 2:3:5:6-Tetrabromaniline (Abstr., 1895, i, 345) can be diazotised by the new method; the solution seems to yield a phenol melting at 246° ; it will yield also a mixture of pentabromobenzene with perbromobenzene; 2:3:5:6-tetrabromobenzonitrile melts at 124° . The three tetrachloranilines can also be diazotised, the 2:3:5:6 isomeride most easily, then the 2:3:4:5, and least easily the 2:3:4:6 isomeride; the derived tetrachlorobenzonitriles melt respectively at 72° , 84° , and 81° .

C. F. B.

Molecular Change of Brominated Diazonium Chlorides into Chlorinated Diazonium Bromides. By ARTHUR R. HANTZSCH, in conjunction with A. SCHLEISSING and M. JAGER (*Ber.*, 1897, 30 2334—2355. Compare Abstr., 1897, i, 408).—Many brominated diazonium chlorides undergo a molecular change, both in the dry state and in solution, by which they pass into chlorinated diazonium bromides. The change of the solid salt is generally accompanied by a partial decomposition of the substance, but in solution no decomposition occurs. The conversion of the chloride into bromide is much more rapid in alcoholic than in aqueous solutions, and is also favoured by concentration and acidity. Compounds containing only one bromine atom do not appear to undergo this remarkable molecular rearrangement, but those in which two atoms are present in ortho- or para-positions relatively to the diazonium group readily change, whilst those with three atoms of bromine react still more rapidly. No instance of the inverse change has yet been observed.

An analogous behaviour is exhibited by the halogen derivatives of the diazonium thiocyanates, which change in a similar manner into thiocyno-diazonium salts.

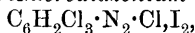
2:4-Dibromodiazonium chloride, $C_6H_3Br_2 \cdot N_2 \cdot Cl$, crystallises with $1H_2O$ in colourless needles, and only changes very slowly in the solid state or in aqueous solution; in alcoholic solution, however, it rapidly passes into 2:4-chlorobromodiazonium bromide, $C_6H_3ClBr \cdot N_2 \cdot Br$, which is a yellow, crystalline powder. When the alcoholic solution of the dibromochloride is saturated with hydrogen chloride, dichlorodiazonium bromide, $C_6H_3Cl_2 \cdot N_2 \cdot Br$, is produced as a microcrystalline powder. 2:4-Dibromorthotoluenediazonium chloride forms a hydrochloride, $3(C_6H_2Br_2Me \cdot N_2 \cdot Cl) + HCl$, which crystallises in readily soluble, colourless needles. The diazonium salt only changes slowly and imperfectly into the corresponding chlorobromo- and dichloro-derivative. When, however, it is treated in alcoholic solution with hydrogen chloride, 2:4-dichlorotoluene, melting at 26.5° , is formed. 2:6-Dibromoparatoluenediazonium chloride closely resembles the ortho-compound, but changes rather more rapidly. When treated in alcoholic solution with hydrogen chloride, 2:6-dichlorotoluene is formed along with chlorobromotoluene. The 2:6-dihalogen toluenediazonium salts occur in two modifications; thus, for instance, dibromotoluenediazonium bromide is obtained in yellow crystals when the alcoholic solution in which the base has been diazotised is immediately treated with ether, whilst, if it be allowed to stand for some time, ether precipitates the salt in brown crystals. These two forms have the same composition, and both explode at $97-98^\circ$. The brown salt becomes yellow when exposed to light, and the yellow salt is obtained when ether is added to the alcoholic solution of the brown salt. 3:5-Dibromodiazonium chloride hydrochloride, $C_6H_3Br_2 \cdot N_2 \cdot Cl, HCl + 4H_2O$, is obtained by diazotising metadibromaniline. When allowed to stand over potash, it passes into the salt, $3(C_6H_3Br_2 \cdot N_2 \cdot Cl), HCl$, whilst the normal diazonium salt is precipitated by the addition of ether to the alcoholic solution. It does not undergo any molecular change into a bromide.

Tribromodiazonium chloride hydrochloride has previously been described. The salt, $3(C_6H_2Br_3 \cdot N_2 \cdot Cl), HCl$, is obtained when the base

is diazotised in solution in acetic acid, or in absolute alcohol at -5° . The normal diazonium salt could not be prepared. The monacid salt changes into a bromide with moderate rapidity, even in the solid state, whilst in aqueous solution the change proceeds at a somewhat slower rate; in alcoholic solution, on the other hand, it proceeds with such rapidity that it is impossible to obtain a precipitate of pure silver chloride by adding silver nitrate to a freshly made solution of the salt. It was found extremely difficult to isolate the actual products formed by this molecular change, but they were all recognised by conversion into the corresponding halogen toluene derivatives. In this way, *symmetrical dibromochlorobenzene*, melting at 96° , *symmetrical dichlorobromobenzene*, and *symmetrical trichlorobenzene* were all obtained. When the monacid tribromodiazonium chloride hydrochloride is suspended in ether, it becomes yellow, but becomes white again as soon as the ether is removed; this behaviour was repeated a second time on similar treatment, but did not occur when the treatment was repeated a third time. The white salt appears to be *chlorodibromodiazonium chloride*, $C_6H_2ClBr_2 \cdot N_2 \cdot Cl$.

Tribromaniline hydrochloride does not undergo any molecular change, so that the reaction appears to be limited to the diazonium salts.

A number of double salts derived from diazonium salts were also examined, but were not found to undergo any similar change. *Tribromodiazonium iodide cadmioidide*, $C_6H_2Br_3 \cdot N_2 \cdot I, CdI_2$, is a dark red salt which becomes yellow and then rapidly decomposes; a second salt, $(C_6H_2Br_3 \cdot N_2 \cdot I_2), CdI_2$, is even less stable. *Trichlorodiazonium chloride dibromide*, $C_6H_2Cl_3 \cdot N_2 \cdot Cl, Br_2$, is a yellow, crystalline mass melting at 136° . *Trichlorodiazonium chloride di-iodide*,



forms reddish-brown crystals which decompose on exposure to light, forming *trichloriodobenzene*, melting at 54° , and *trichlorodiazonium iodide dichloride*, which crystallises in light yellow prisms melting at 156° . *Trichlorodiazonium chloride bromide iodide*, $C_6H_2Cl_3 \cdot N_2 \cdot Cl, Br, I$, is formed in orange-red crystals melting at 132° , when the chloride is treated in alcoholic solution with iodine bromide.

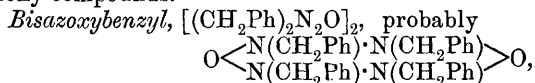
Hexachlorodiazoamidobenzene, prepared by the diazotisation of trichloraniline, crystallises in very small, white needles, which decompose at 141° . *Hexabromodiazoamidotoluene* is a white, spongy mass.

A. H.

Alaryl- and Alkyl-Hydroxylamines. By EUGEN BAMBERGER and EDMOND RENAULD (*Ber.*, 1897, 30, 2278—2289).—Azoxy-compounds can be readily obtained by the action of nitrosobenzene on β -alaryl-hydroxylamines. The authors have obtained theoretical yields of the following: metazoxytoluene (37°), parazoxytoluene (69°), paradichlorazoxybenzene (154°), metadibromazoxybenzene (109 — 110°), and paradibromazoxybenzene (169 — 170°). Nitroso- and hydroxylamine compounds which contain different alaryl groups yield a mixture of the two simple azoxy-derivatives, for example, $NO \cdot Ph$ and $C_6H_4Me \cdot NH \cdot OH$ give $Ph \cdot N_2O \cdot Ph$ and $C_6H_4Me \cdot N_2O \cdot C_6H_4Me$.

Alkylated hydroxylamines, for example β -benzylhydroxylamine,

react in a different manner, and yield substances polymeric with the azoxy-compounds.



is obtained when pure β -benzylhydroxylamine (7.3 grams) is gradually added to a cooled solution of nitrosobenzene (9.5 grams) in absolute alcohol. It crystallises from boiling xylene in nodular groups of needles melting at $210-211^\circ$, and is but sparingly soluble in boiling alcohol or ether. α -Naphthylamine, added to a cold acetic acid solution of the compound, gives an intense violet-red coloration. The compound yields an orange-red colour when added to heated phenol, but does not give Liebermann's reaction. Other products are formed in addition to bisazoxybenzyl by the action of nitrosobenzene on benzylhydroxylamine; among these are azoxybenzene, azobenzene, aniline, benzaldehyde, crystals melting at $200-202^\circ$, others at 160° and a red oil.

Phenylazohydroxymethylamide,* $\text{PhN}_2 \cdot \text{NMe} \cdot \text{OH}$, is formed when a sodium acetate solution of diazobenzene chloride is slowly added to an acetic acid solution of β -methylhydroxylamine at 0.5° (compare Abstr., 1896, i, 222). It is readily soluble in the usual solvents, with the exception of light petroleum, crystallising from the latter in white, glistening needles melting at $69-70^\circ$. With alcoholic copper acetate, it yields a brownish-red precipitate of the normal copper derivative $(\text{N}_2\text{Ph} \cdot \text{NMeO})_2\text{Cu}$, which, after recrystallisation from boiling alcohol, forms dark, brownish-red needles possessing a bronzy lustre. When allowed to crystallise slowly, it forms glistening black prisms of high specific gravity. The azohydroxamide is readily hydrolysed by mineral acids.

Paranitrophenylazohydroxymethylamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{NMe} \cdot \text{OH}$, crystallises from boiling alcohol in glistening, yellow needles, and melts at 231° . It is only sparingly soluble in cold benzene, chloroform, or alcohol, but dissolves in alkalis, giving deep-red solutions.

Paranitrophenylazomethoxymethylamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{NMe} \cdot \text{OMe}$, obtained by the action of alcohol and methylic iodide on the previous compound, crystallises from light petroleum in glistening, brownish-yellow needles melting at 142° .

Paranitrophenylazohydroxybenzylamide crystallises in golden-yellow plates with a bronzy lustre. It melts at $181-182^\circ$, and is readily soluble in benzene. *Phenylazohydroxybenzylamide* forms needles melting at 105° ; *paratolylazohydroxybenzylamide*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{N}(\text{OH}) \cdot \text{CH}_2\text{Ph}$, crystallises in long, silky needles melting at 106.5° . *Paranitrophenylazob-hydroxyamidopropionic acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{N}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, crystallises in small, brownish-red needles melting at $177-178^\circ$. All these compounds yield characteristic copper derivatives.

α -Benzylhydroxylamine reacts with paranitrodiazobenzene acetate, yielding paranitrodiazobenzoimide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_3$ (m. p. 71°), benzylic alcohol, and water. Orthonitrodiazobenzoimide (52°) and orthonitroparadiazotoluimide (69°) were obtained in a similar manner.

J. J. S.

* The author uses the expression azoamide in place of the usual nomenclature diazoamido-compound; Hantzsch has suggested diazoamide.

N-Alkylhydroxylamines. By ERNST O. BECKMANN (*J. pr. Chem.*, 1897, [ii], 56, 71—93).—When a β -hydroxylamine, $\text{NHR}\cdot\text{OH}$, is treated with phenylcarbimide, $\text{NPh}\cdot\text{CO}$, in benzene solution, the product is $\text{NPh}\cdot\text{CO}\cdot\text{NR}\cdot\text{OH}$, and, when heated with a chloride RCl in the presence of alcoholic sodium ethoxide, it yields the compound $\text{NPh}\cdot\text{CO}\cdot\text{NR}\cdot\text{OR}$. That this is the mechanism of the reaction is evident from the fact that the same final product is obtained starting with the α -hydroxylamine, the intermediate product being different: $\text{NH}_2\cdot\text{OR}\rightarrow\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{OR}\rightarrow\text{NPh}\cdot\text{CO}\cdot\text{NR}\cdot\text{OR}$. This final product is, moreover, different from the isomeric compound, $\text{NR}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, obtained by treating the di- β -hydroxylamine, $\text{NR}_2\cdot\text{OH}$, with phenylic isocyanate.

Compounds of the type $\text{NPhCO}\cdot\text{NR}\cdot\text{OBz}$, when heated, frequently undergo a molecular transformation into others of the type $\text{NRBz}\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$. Thiocarbimides also add themselves on to β -hydroxylamines, but under certain circumstances the product is a thiocarbamide, oxygen being lost.—The presence of an OH group in these hydroxylamine derivatives conditions their solubility in alkalis, and a colour reaction with ferric chloride. The following is a list of the compounds described (the numbers quoted are melting points).

[With B. GOETZE].—N-Benzylformaldoxime, 116° ; N-benzylpropionaldoxime, 106° ; N-benzylöenanthaldoxime, 85° ; $\text{CH}_2\text{Ph}\cdot\text{N}\begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix} \text{CHR}$.

[With F. SCHÖNERMARK].— β -Carbanilido- β -benzylhydroxylamine, $\text{NPh}\cdot\text{CO}\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{OH}$, 163° ; its *methylic*, 87° ; *ethylic*, 74° ; *benzylic*, 107° ; *benzoyl*, 120° , and *phenylsulphonic*, 120° , derivatives, $\text{NPh}\cdot\text{CO}\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{OR}$. α -Carbanilido- β -dibenzylhydroxylamine, $\text{N}(\text{CH}_2\text{Ph})_2\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, 117° . α -Carbanilido- β -benzoyl- β -benzylhydroxylamine, $\text{NBz}(\text{CH}_2\text{Ph})\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, 140° .

[With HEINRICH KÖNIG].— β -Anisylhydroxylamine, $\text{OMe}\cdot\text{C}_7\text{H}_6\cdot\text{NH}\cdot\text{OH}$, 76° ; its hydrochloride, 167° ; its β -carbanilido-derivative,

$\text{NPh}\cdot\text{CO}\cdot\text{N}(\text{C}_7\text{H}_6\cdot\text{OMe})\cdot\text{OH}$, 161° ; and its *methylic*, 103° ; *ethylic*, 92° ; *benzylic*, 85° ; and *benzoyl*, 134° , derivatives. α -Carbanilido- β -benzoyl- β -anisylhydroxylamine,

$\text{NBz}(\text{C}_7\text{H}_6\cdot\text{OMe})\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, 92° ; $\alpha\beta$ -dibenzoyl- β -anisylhydroxylamine, $\text{NBz}(\text{C}_7\text{H}_6\cdot\text{OMe})\cdot\text{OBz}$, 64° .

[With F. SCHÖNERMARK].— β -Carbanilido- β -phenylhydroxylamine, $\text{NPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{OH}$, 125° ; and its *methylic*, 74° ; and *benzoyl*, 100° , derivatives. α -Carbanilido- β -benzoyl- β -phenylhydroxylamine,

$\text{NPhBz}\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, 127° . α -Benzoyl- β -phenylhydroxylamine, $\text{NPhBz}\cdot\text{OH}$, 120 — 121° ; $\alpha\beta$ -dibenzoyl- β -phenylhydroxylamine, $\text{NPhBz}\cdot\text{OBz}$, 118 — 119° . β -Thiocarbanilido- β -benzylhydroxylamine, $\text{NPh}\cdot\text{CS}\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{OH}$, 131 — 132° . Thiocarbanilido, 111° ; thiocarballylamido-, 98° ; and thiocarbomethylamido-, 146° ; β -phenylhydroxylamines, $\text{NPh}\cdot\text{CS}\cdot\text{NR}\cdot\text{OH}$.

C. F. B.

Nitro-substituted Hydroxamic Acids. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1897, 16, 184—188).—Paranitrobenzoic chloride reacts with benzhydroxamic acid, yielding paranitrobenzoylbenz-

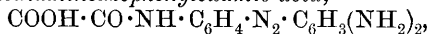
hydroxamic acid, a compound identical with that obtained by the action of nitrobenzoic chloride on the sodium derivative of phenylnitromethane. Benzoic chloride and paranitrobenzhydroxamic acid yield benzoyl-paranitrobenzhydroxamic acid, which is identical with the product obtained by the action of benzoic chloride on the potassium derivative of paranitrophenylnitromethane (compare Abstr., 1897, i, 409).

A mixture of *nitrobenzhydroxamic acid* and *dinitrobenzhydroxamic acid* is obtained by the action of paranitrobenzoic chloride on hydroxylamine; the two may be separated by the action of sodium carbonate solution, which dissolves the mononitro-acid only. The dinitro-acid crystallises from alcohol in pale yellow plates decomposing at 174° ; it dissolves slowly in potassium hydroxide solution, and when its alkaline solution is boiled paranitraniline is formed. The mononitro-acid is best obtained by dissolving in glacial acetic acid and adding benzene; it decomposes at 171° and dissolves readily in potassium hydroxide.
J. J. S.

Bismarck-brown. By ERNST TÄUBER and FRANZ WALDER. (*Ber.*, 1897, 30, 2111—2117).—When Bismarck-brown is prepared by the action of sodium nitrite on metaphenylenediamine dihydrochloride, nitrogen is evolved. When the monhydrochloride is employed, on the other hand, the reaction is not complete, although no gas is evolved. Finally, when 4 molecules of acid are used for 2 of the base, the latter is completely converted into colouring matter, without the evolution of gas. In no case is triamidoazobenzene the sole product, whilst many samples of Bismarck-brown, prepared in the laboratory and also on the large scale, do not contain any of the triamido-compound. Pure triamidoazobenzene is best prepared from its *monacetyl* derivative, which is obtained by diazotising monacetometaphenylenediamine and bringing the resulting salt into reaction with metaphenylenediamine. It forms brick-red, lustrous plates melting at 165° , and when hydrolysed yields triamidoazobenzene, which crystallises with $\frac{1}{2}$ mol. of benzene in plates melting at 143 — 145° . These belong to the monosymmetric system, the constants being $a : b : c = 1.1804 : 1 : 1.7966$; $\beta = 84^{\circ} 52'$.

Another substance which is contained in many samples of the colouring matter is a *disazo-compound*, the exact constitution of which has not yet been ascertained. It may be extracted from the base of the colouring matter by benzene, from which it crystallises with $\frac{2}{3}$ mol. of benzene and melts at 118° . When recrystallised from a mixture of benzene and phenol, it separates with 1 mol. of phenol, and then melts at 136° . The base has the composition $C_{18}H_{18}N_8$, and is insoluble in water.
A. H.

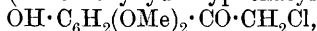
Bismarck-brown. By RICHARD MÖHLAU and LUDWIG MEYER (*Ber.*, 1897, 30, 2203—2206).—In order to prove the correctness of Caro and Griess's statement, that the chief product of the action of sodium nitrite on metaphenylenediamine hydrochloride is triamidoazobenzene, the authors prepared this compound by combining diazotised phenyloxamic acid with metaphenylenediamine and hydrolysing the product.

Metaphenylenediamineazophenylloxamic acid,

separates from its hot, ammoniacal solution in dark red prismatic crystals on adding excess of dilute acetic acid; it decomposes at 189° without melting, and yields triamidoazobenzene on hydrolysis with dilute sulphuric acid. The hydrochloride of triamidoazobenzene contains 2 mols. of hydrochloric acid to 1 mol. of the base, which is in accordance with Caro and Griess's work; further, it appears to crystallise with $1\text{H}_2\text{O}$. The melting point, 143.5° , is also in agreement with that found by the above investigators, the *triacetyl* compound crystallises from absolute alcohol in yellow needles melting at 264° .

J. F. T.

Some Ketones of the Phloroglucinol Series. (Researches on the Flavone Derivatives. VII.). By PAUL FRIEDLÄNDER and LUDWIG C. SCHNELL (*Ber.*, 1897, 30, 2150—2155. Compare Abstr., 1897, i, 442, 482.).—The authors carried out the following experiments with the hope of preparing symmetrical trihydroxyacetophenone from which flavone derivatives might be obtained of a character similar to those which occur in nature. Trimethylphloroglucinol is best obtained by the distillation of the residues of coto bark with caustic soda, after treating them with methylic iodide and an alkali. Trimethylphloroglucinol is converted by acetic chloride, in the presence of aluminium chloride, into di- and tri-methylphloracetophenone. *Dimethylphloracetophenone*, $\text{OH} \cdot \text{C}_6\text{H}_2(\text{OMe})_2\text{Ac}$, which is the chief product when the residue first obtained is heated with aluminium chloride, crystallises in slender needles, melting at 85 — 88° . *Trimethylphloracetophenone* crystallises in almost colourless, striated prisms melting at 97 — 98° . *Dimethylphloracetophenone chloride* (dimethoxyhydroxyphenacyl chloride),



is obtained by heating trimethylphloroglucinol with chloracetic chloride and aluminium chloride, the residue which is formed being finally heated with an excess of aluminium chloride; it crystallises in slender, colourless needles melting at 142 — 144° , and in alcoholic solution is coloured an intense violet by ferric chloride. *Dimethoxyketocoumaran*, $\text{C}_6\text{H}_2(\text{OMe})_2 \text{---} \text{C}(\text{O}) \text{---} \text{CH}_2$, obtained by warming the foregoing compound, in a fine state of division, with sodium carbonate for a very short time, crystallises in colourless needles melting at 136 — 138° . Both the acetophenone chloride and the ketocoumaran readily condense with aldehydes. Benzaldehyde yields a substance of the composition of a *dimethylchrysin*, $\text{C}_{15}\text{H}_8\text{O}_2(\text{OMe})_2$, which crystallises in almost colourless needles melting at 150 — 152° , but is not identical with the compound obtained by Picard by the methylation of monomethylchrysin. Piperonal yields a *compound*, which separates from alcohol in small, yellow crystals melting at 220 — 224° . Furfuraldehyde also yields a condensation *product*, which crystallises in yellow glistening needles melting at 177 — 179° . The *compound* formed with protocatechuic aldehyde colours alumina mordants orange-yellow, and chrome mordants yellowish-brown, the shades being markedly more yellow than those produced by the product obtained from the unsubstituted ketocoumaran and the same aldehyde.

A. H.

Paramidobenzaldehyde. By REINHOLD WALTHER and O. KAUSCH (*J. pr. Chem.*, 1897, [ii] 56, 97—123).—*Paramidobenzylidenephénylhydrazone*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{N} \cdot \text{NHPh}$, prepared by the action of phenylhydrazine on paramidobenzaldehyde in acetic acid solution, crystallises from alcohol in glistening, yellow leaflets melting at 175° . It is insoluble in water and light petroleum, but soluble in mineral acids, alcohol, and benzene. The *monacetyl* derivative crystallises in yellow leaflets melting at 155° , the *diacetyl* derivative in yellow needles melting at 211° ; and the *benzoyl* derivative in yellow leaflets melting at 159 — 160° .

Aromatic aldehydes react with paramidobenzylidenephénylhydrazone with elimination of water, giving rise to compounds containing the complex $-\text{CH}:\text{N}-$ twice: *benzylideneparamidobenzylidenephénylhydrazone* crystallises from benzene in yellow, microscopic needles melting at 140° , and *orthohydroxybenzylideneparamidobenzylidenephénylhydrazone* in beautiful, yellow, glistening leaflets melting at 173 — 174° . The hydrazone also reacts with the thiocarbimides; in the case of phenylthiocarbimide, *parabenzylidenephénylhydrazonethiocarbamil* is produced which separates from alcohol in yellow, microscopic crystals melting at 220 — 221° ; allylthiocarbimide gives *parabenzylidenephénylhydrazone-allylthiocarbamide* crystallising from alcohol in yellowish-white leaflets melting at 136° .

When paramidobenzylidenephénylhydrazone is heated in sealed tubes with carbon bisulphide, a compound is formed which crystallises in yellow needles and melts at 220° ; it appears to be *dibenzylidenephénylhydrazonethiocarbamide*, $\text{SC}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{N} \cdot \text{NHPh})_2$.

The action of ethylic acetoacetate on paramidobenzylidenephénylhydrazone was investigated, but the results were unsatisfactory, mainly owing to the insolubility of the substances formed.

Paramidobenzylideneaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{NPh}$, may be obtained either by the action of aniline or aniline hydrochloride on paramidobenzaldehyde. It separates from alcohol in yellow leaflets and from ether in yellow needles melting at 110° . It is insoluble in alkalis, but dissolves in acids, and on boiling with them is decomposed into its components. When acted on by carbon bisulphide, a yellowish-green substance is produced which could not be further investigated on account of its insolubility in all menstrua.

Paramidobenzaldoxime, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{N} \cdot \text{OH}$, prepared by the action of hydroxylamine hydrochloride on paramidobenzaldehyde, separates from hot water in yellow crystals melting at 124° .

Diparamidodibenzylidenehydrazone, $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, obtained when hydrazine sulphate is gradually added to paramidobenzaldehyde, crystallises from alcohol in yellow leaflets melting at 245° .

Paramidobenzylidenediparamidoazobenzene,



is obtained by the interaction of paramidoazobenzene and paramidobenzaldehyde. It crystallises from dilute alcohol in red needles melting at 115° , and dissolves in acids with a red coloration. When reduced with zinc dust and acetic acid in alcoholic solution, it is converted into the insoluble modification of paramidobenzaldehyde, aniline, and paraphenylenediamine being also produced.

Diazoamidobenzaldehyde, $\text{COH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}:\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COH}$, obtained

by the action of sodium nitrite (1 mol.) on paramidobenzaldehyde (2 mols.) in acetic acid solution, crystallises from light petroleum in golden-yellow leaflets melting at 135° . It may be converted into the corresponding amidoazo-compound.

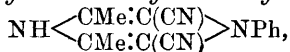
Diazobenzaldehyde may be prepared by the ordinary method; it was not isolated, but proved to exist in the solution, for, on boiling, nitro-parahydroxybenzaldehyde was obtained. Diazobenzaldehyde reacts with amines; the *aniline* compound crystallises from alcohol in yellow leaflets melting at 157° , the *paratoluidine* compound in reddish-brown leaflets melting at 145° , and the *paraphenylenediamine* compound in violet leaflets having no definite melting point. The last named is soluble in sulphuric acid with a beautiful blue-violet coloration, and in hydrochloric acid giving a rose-red solution, but is insoluble in benzene, chloroform, acetone, and water.

Parahydroxybenzeneazobenzaldehyde, $\text{COH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, formed by the action of phenol on a solution of diazobenzaldehyde, crystallises from alcohol in glistening red leaflets melting at 195° ; it dissolves in alkalis giving a carmine-red solution, whilst with sulphuric acid a dark, orange coloured solution is produced. *Dihydroxybenzeneazobenzaldehyde*, $\text{COH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{OH})_2$. $[(\text{OH})_2 = 1 : 3]$, prepared from resorcinol and diazobenzaldehyde, forms red crystals which do not melt at 300° .

Diazobenzaldehyde also combines with salicylic aldehyde to form a substance crystallising in yellow leaflets melting at 180° . A. W. C.

Action of Diacetonitrile on Aldehydes. By ERNST MOHR (*J. pr. Chem.*, 1897, **56**, 124—142).—*Benzylidenediamidocrotononitrile* or *benzylidenedi-imidoacetacetonitrile*, $\text{CHPh}[\text{C}(\text{CN}) \cdot \text{CMe} \cdot \text{NH}_2]_2$ or $\text{CHPh}[\text{CH}(\text{CN}) \cdot \text{CMe} \cdot \text{NH}]_2$. When benzaldehyde is acted on by diacetonitrile, a substance of the composition $\text{C}_{15}\text{H}_{16}\text{N}$ is produced. The author has not been able to decide which of the above constitutional formulæ it possesses, but hopes shortly to satisfactorily prove this point. The same remark applies to the condensation products of diacetonitrile with other aldehydes, mentioned in this abstract. The compound crystallises from absolute alcohol in prisms melting at 190° with partial decomposition and evolution of gas. It is almost insoluble in benzene and ether, but readily soluble in water and absolute alcohol.

3 : 5-Dicyano-4-phenyl-2 : 6-dimethyl-1 : 4-dihydropyridine,



is produced with elimination of ammonia when benzylidenediamidocrotononitrile is treated with concentrated hydrochloric acid, acetic anhydride, or sulphuric acid. It separates from alcohol as a yellowish, crystalline powder melting at 204 — 206° . It remains unchanged after heating at 105° for some hours, is easily soluble in acetic acid and caustic soda, and sparingly in dilute hydrochloric or sulphuric acids; it is remarkable that the solution in hot hydrochloric acid or sodium hydroxide is deep yellow, and on cooling, the substance crystallises out, leaving the mother liquor colourless.

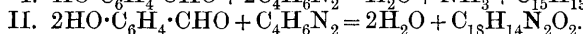
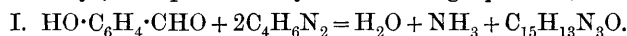
Paramethoxybenzylidenediamidocrotononitrile or *paramethoxybenzyl-*

denedi-imidoacetoacetonitrile, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}[\text{C}(\text{CN}) : \text{CMe} \cdot \text{NH}_2]_2$ or $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}[\text{CH}(\text{CN}) \cdot \text{CMe} \cdot \text{NH}]_2$, is obtained when anisaldehyde is gradually added to diacetonitrile suspended in benzene. It crystallises from water in snow-white prisms, and from alcohol in long needles sparingly soluble in benzene or ether. When quickly heated, it melts at $188-192^\circ$, but on slowly heating, the greater portion melts at $155-160^\circ$; in this case, it becomes yellow, and between 175 and 180° evolves gas.

3:5-Dicyano-4-paramethoxyphenyl-2:6-dimethyl-1:4-dihydropyridine, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{C}(\text{CN}) : \text{CMe} \\ \text{C}(\text{CN}) : \text{CMe} \end{smallmatrix} \text{NH}$, is obtained in snow-white needles melting at $215-216^\circ$, when acetic anhydride acts on paramethoxybenzylidenediamidocrotononitrile. It is soluble in alcohol and chloroform, but only sparingly so in ether, benzene, and light petroleum.

Metanitrobenzylidenediamidocrotononitrile (*metanitrobenzylideneacetoacetonitrile*) crystallises from alcohol in yellow, transparent prisms melting at $118-120^\circ$; the corresponding *piperonylidene* compound separates from alcohol in needles melting at 210° ; and the *cinnamylidene* compound in compact prisms melting at $149-159^\circ$; the latter is coloured red on exposure to air.

The condensation of salicylaldehyde with diacetonitrile takes place in two ways, as represented by the following equations,



The compound produced according to reaction I is,

3:5-Dicyano-4-orthohydroxyphenyl-2:6-dimethyl-1:4-dihydropyridine; it crystallises from absolute alcohol in colourless, glistening, transparent four-sided prisms. When heated to $230-240^\circ$, it turns yellow, and melts between $265-270^\circ$, becoming black.

The compound $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ crystallises from alcohol in colourless needles melting at $179-180^\circ$, but the author has been unable to decide its constitution. When treated with acetic anhydride, ammonia is not eliminated, but a *monacetyl* derivative is produced crystallising from a mixture of dry benzene and light petroleum and melting at 170° . It is very unstable, readily giving up the acetyl group, the original substance being regenerated.

When the compound $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$, in glacial acetic acid solution, is boiled with hydrochloric acid, a *polyacetyl* derivative is obtained crystallising from glacial acetic acid in colourless needles melting at $209-211^\circ$; like the monacetyl derivative, it is very unstable.

A. W. C.

Action of Benzaldehyde on Ketones. By DANIEL VORLÄNDER (*Ber.*, 1897, 30, 2261—2268. Compare *Abstr.*, 1896, i, 546 and 603, Petrenko-Kritschenko, *ibid.*, i, 472). Dipropyl ketone (40 grams), benzaldehyde (37 grams), alcohol (300 c.c.), water (200 c.c.) and 10 per cent. sodium hydroxide solution (40 c.c.) are mixed together and allowed to stand in a stoppered vessel for some 30 days, care being taken that the mixture is well shaken from time to time. The oil which is obtained when the ether is distilled from the ethereal extract is subjected to distillation under a pressure of 40 mm., when the

following fractions are obtained: 100—107°, about 14.8 grams, consisting mainly of benzaldehyde; 150—170°, 4 grams; 170—190°, about 13.7 grams, consisting mainly of *benzylidenedipropyl ketone*, $\text{CHPh}:\text{C}(\text{Et})_2:\text{CO}:\text{CH}_2\text{Et}$, and 200—235°, about 8 grams of a syrupy oil consisting of *diphenyldiethylhydropyrone*, $\text{CO} < \begin{smallmatrix} \text{CHEt} \cdot \text{CHPh} \\ \text{CHEt} \cdot \text{CHPh} \end{smallmatrix} > \text{O}$.

No better yield of these two compounds can be obtained by using 2 mols. of benzaldehyde to 1 of the ketone. The author attributes the poor yield, as compared with the corresponding reaction between benzaldehyde and diethyl ketone, to stereochemical influences. Benzylidenedipropyl ketone is a colourless oil distilling at 176—178° under a pressure of 40 mm.; it is readily miscible with alcohol or ether and alcohol, and reacts with methylic malonate in the presence of a small quantity of sodium methoxide, yielding *methylic phenyldiethylhydroresorcyate*, $\text{CO} < \begin{smallmatrix} \text{CHEt} - \text{CO} \\ \text{CHEt} \cdot \text{CHPh} \end{smallmatrix} > \text{CH} \cdot \text{COOMe}$, which crystallises in prisms melting at 139°. The yield is good. *Phenyldimethylhydroresorcylic acid*, obtained by allowing its methylic salt (Abstr., 1896, i, 546) to remain in contact with an excess of aqueous alcoholic potash for 10 days, crystallises in colourless crystals; it melts at 124°, and is at the same time converted into *phenyldimethylhydroresorcinol*. This melts at 190—192° to a yellow liquid, and gives a brownish coloration with ferric chloride.

Benzaldehyde reacts with an aqueous alcoholic solution of suberone in the presence of sodium or potassium hydroxide, the only product being Wallach's dibenzylidenesuberone (Abstr., 1896, i, 572); this readily combines with 4 atoms of bromine, yielding an *additive* compound which melts and decomposes at 185°.

Benzaldehyde does not react with pinacone under the conditions given above. It is stated that pinacone is not transformed into pinacolin by boiling with concentrated sodium carbonate, or by heating with water at 120—130°. The transformation, however, can easily be accomplished by boiling with a 5 per cent. oxalic acid solution for 12 hours, or by boiling for 3—4 hours with a 50 per cent. solution of tartaric, phosphoric, or oxalic acid. Benzaldehyde and methyl propyl ketone yield an oily benzylidene derivative and a complex crystalline compound melting at 197°; the latter is neither a simple dibenzylidene derivative nor yet a hydrophorone. Phorone and mesityloxide both react with benzaldehyde in the presence of sodium hydroxide, yielding complex amorphous compounds. J. J. S.

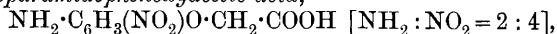
Benzylidenepinacolin. By DANIEL VORLÄNDER and FRITZ KALKOW (*Ber.*, 1897, 30, 2268—2274. Compare preceding abstract).—A theoretical yield of *benzylidenepinacolin*, $\text{CHPh}:\text{CH}:\text{CO}:\text{CMe}_3$, is obtained when a mixture of benzaldehyde (21.2 grams), pinacolin (20 grams), alcohol (75 c.c.), water (25 c.c.), and 10 per cent. sodium hydroxide solution (20 c.c.) is allowed to stand for 9 days. It crystallises from aqueous alcohol in flat prisms melting at 41°, and is soluble in alcohol, ether, benzene, chloroform, and light petroleum. A compound, $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2$ (probably benzylidenepinacolinoxime + hydroxylamine), is obtained when an aqueous alcoholic solution of benzylidenepinacolin

(1 mol.) is boiled with hydroxylamine hydrochloride (4—5 mols.) and the requisite quantity of soda for 8 hours. It crystallises in colourless needles, melts at 145—146°, is readily soluble in dilute hydrochloric acid or in sodium hydroxide solution, also in ether, benzene, or chloroform, is almost insoluble in water, and reduces Fehling's solution in the cold. A δ -ketonic acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CMe}_3$, is obtained by the combination of benzylidenepinacolone with ethylic malonate in the presence of sodium ethoxide and the subsequent elimination of a molecule of carbonic anhydride it crystallises from boiling water in needles melting at 124°. The *oxime*, $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$, of the ketonic acid crystallises in flat prisms, melts at 131°, and has an acid reaction. The *amide*, $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}$, obtained by the action of concentrated aqueous ammonia on the acid anhydride, crystallises from boiling water or from benzene in flat needles melting at 133°. Bromine readily reacts with a chloroform solution of benzylidenepinacolin, yielding a *dibromide*, $\text{CHPhBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CMe}_3$, which crystallises from boiling alcohol in large prisms melting at 124°. A β -diketone, $\text{COPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CMe}_3$, and not the acetylene derivative, $\text{CPh} : \text{C} \cdot \text{CO} \cdot \text{CMe}_3$, is formed by the action of alcoholic potash on the dibromide. It is a colourless oil distilling at 161—165° under a pressure of 25 mm.; when treated with bromine in chloroform solution, it yields a monobromo-derivative, $\text{COPh} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CMe}_3$, crystallising in glistening prisms and melting at 106°. The diketone (3 grams), when heated for 5 hours on the water bath with phenylhydrazine (2 grams) and glacial acetic acid (5 c.c.) yields a *pyrazole* derivative, $\text{CH} \begin{smallmatrix} \diagup \text{C}(\text{CMe}_3) \cdot \text{NPh} \\ \diagdown \text{CPh} = \text{N} \end{smallmatrix}$ or $\text{CH} \begin{smallmatrix} \diagup \text{C}(\text{CMe}_3) : \text{N} \\ \diagdown \text{CPh} = \text{NPh} \end{smallmatrix}$. This crystallises in colourless prisms, melts at 77°, distils at 229—231° under a pressure of 25 mm., and is insoluble in dilute acids or alkalis. On boiling with concentrated potassium hydroxide, the diketone is decomposed into acetophenone and trimethylacetic acid.

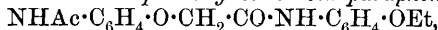
The author considers that his results confirm the usual constitution ascribed to pinacolin, and thinks that but slight importance should be attached to Delacro's criticisms (Abstr., 1896, i, 591, 602), since zinc alkyl syntheses are not always trustworthy. J. J. S.

Derivatives of Paramidophenoxyacetic Acid. By CURTIS C. HOWARD (*Ber.*, 1897, 30, 2103—2107. Compare Abstr., 1897, i, 283).—The *hydrazone* of benzylideneparaphenoxyacetic acid, $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$, formed when benzaldehyde reacts with hydrazidoparaphenoxyacetic acid in alcoholic solution, crystallises from dilute alcohol in greenish-yellow scales melting at 158°, the *tartrazine* dye from hydrazidoparaphenoxyacetic acid is formed when the latter is treated with sodium dihydroxytartrate, and is obtained in orange-red crystals melting at 242°. On heating the hydrazido-acid with ethylic acetoacetate in alcohol solution, *methylpyrazoloneparaphenoxyacetic acid*, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_4$, is produced, which crystallises from dilute alcohol in white needles melting at 211°; the *methylic* salt is an oil. *Orthometadinitroparacetamidophenoxyacetic acid*, $\text{NHAc} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$, obtained by the nitration of paracetamidophenoxyacetic acid, crystallises from hot water in yellow crystals melting at 205°, and on reduction gives

the anhydride of *μ-methylmetamidoparaphenoxyacetic acid imidazole*, which crystallises from alcohol in glistening plates melting at 243°. *Orthonitroparamidophenoxyacetic acid*,



is formed when paramidophenoxyacetic acid in concentrated sulphuric acid solution is treated with the theoretical quantity of potassium nitrate; it crystallises from water in brown prisms melting at 196°, and on reduction gives *orthoparadiamidophenoxyacetic anhydride*, which crystallises from water in thin prisms melting at 225°, the ethylic salt melts at 58°. *Paracetamidophenoxyacetic acid paraphenetide*,



from paracetamidophenoxyacetic acid and paraphenetidine, crystallises from dilute acetic acid in microscopic crystals melting at 198°.

J. F. T.

The Nitration of Coumarone. By RICHARD STOERMER and O. RICHTER (*Ber.*, 1897, 30, 2094—2096).—Coumarone readily reacts with concentrated nitric acid, with the production of two isomeric nitro-derivatives, and also of 5-nitrosalicylic acid. *Paranitrocoumarone*, $\text{C}_8\text{H}_5\text{O} \cdot \text{NO}_2$, crystallises in yellow, glistening needles melting at 134°, and *orthonitrocoumarone* in yellow needles melting at 85°. The monohalogen derivatives of coumarone likewise yield nitro-derivatives, thus, from bromocoumarone, *nitrobromocoumarone*, $\text{C}_8\text{H}_4\text{OBr} \cdot \text{NO}_2$, is produced, and from chlorocoumarone, *nitrochlorocoumarone*, $\text{C}_8\text{H}_4\text{OCl} \cdot \text{NO}_2$, the former separating from dilute alcohol in glistening needles melting at 132°; and the latter in yellow needles melting at 147°. J. F. T.

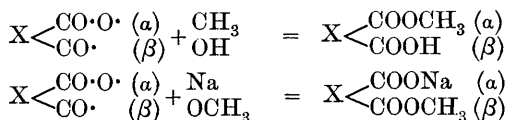
Action of Hübl's Reagent on Gallic and Tannic Acids. By CARL BOETTINGER (*Chem. Zeit.*, 1896, 20, 984—985).—Under similar conditions, gallic acid reacts with a larger quantity of the reagent than does tannic acid. With gallic acid, a golden-yellow substance is obtained which is readily soluble in water; with tannic acid, a yellow granular precipitate which is almost insoluble in water. Both substances give up iodine readily. The reaction with both acids takes place much more readily when concentrated solutions of Hübl's reagent are employed.

J. J. S.

Production of Acid Ethereal Salts from Acid Anhydrides. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, 18, 418—432. Compare Abstr., 1895, i, 420).—The author has previously stated the view that, by the action of alcoholic sodium derivatives on the anhydrides of unsymmetrical dibasic acids, ethereal salts are produced different from those formed by the action of alcohol alone. As the only observation of this description made on camphoric anhydride (Bredt, *Annalen*, 1896, 292, 98) does not agree with this supposition, the author has studied the action of sodium methoxide on hemipinic anhydride. He finds that when this substance is acted on by sodium methoxide in presence of methylic alcohol or benzene, both the α - and β -salts are produced in considerable quantities; the production of the β -salt increases the less alcohol or water is present. In the absence of disturbing secondary reactions, the β -salts form a normal product of the action of alcoholic sodium derivatives on acid anhydrides. The β -methylic salt

of hemipinic acid is not to any considerable extent converted into the α -salt by the action of sodium methoxide.

These facts are to be expected if Ostwald's hypothesis, that chemical reactions take place between ions, be accepted. The ions of sodium methoxide are Na and OCH_3 and of methylic alcohol OH and CH_3 : so that if one supposes an anhydride group always splits in the same manner, the following equations will represent the changes which take place.



The author finds that the α -methylic salt of hemipinic acid exists in two stereoisomeric forms, the one melting at $121-122^\circ$, and the other at 138° . Details of the work will be given later.

A. W. C.

Intramolecular Rearrangement of Sulphonic Acids. II. By EUGEN BAMBERGER and JAC. KUNZ (*Ber.*, 1897, 30, 2274—2277. Compare Abstr., 1897, i, 286).—The potassium salt of phenylsulphonamic acid is readily transformed into orthamidobenzenesulphonic acid if it is mixed with acetic acid containing a few drops of sulphuric acid and kept at 0° for about 80 hours. The ortho-acid is converted into the isomeric paramidobenzenesulphonic acid when heated with sulphuric acid at $180-190^\circ$ for 7 hours.

J. J. S.

Condensation with Phenylacetone. By GUIDO GOLDSCHMIEDT and GUSTAV KNÖPFER (*Monatsh.*, 1897, 18, 437—446).—When the product of the condensation of phenylacetone with benzaldehyde in presence of potassium hydroxide is repeatedly recrystallised from alcohol, two substances are produced, one melting at 71° and the other at 153° .

The substance melting at 71° has the formula $\text{C}_{16}\text{H}_{14}\text{O}$, and must be either *benzyl styryl ketone*, $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$, or *stilblyl methyl ketone*, $\text{CH}_3 \cdot \text{CO} \cdot \text{CPh} \cdot \text{CHPh}$. It is easily soluble in alcohol, ether, and benzene, and on treatment with alkalis appears to be reconverted into its constituents. It reacts with hydroxylamine, yielding a substance melting at $102-103^\circ$ and easily soluble in alcohol, ether, or benzene, but with difficulty in water. It is insoluble in acids and alkalis, and after boiling with acetic anhydride, the unchanged substance is precipitated by water, pointing to the fact that it is not an oxime, but a substance which has undergone an isomeric change, such a change having been previously noticed in the case of unsaturated ketones (compare Gattermann and Stockhausen, Abstr., 1893, i, 164, and Knoevenagel and Klages, Abstr., 1895, i, 48).

The substance melting at 153° crystallises from alcohol in beautiful, glistening crystals of which the constitution has not yet been definitely decided, but it seems probable that it is *triphenyltetrahydro- γ -pyrone*.

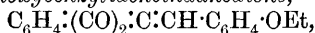
When hydrochloric acid is used as the condensing agent in place of potassium hydroxide, a substance of the composition $\text{C}_{16}\text{H}_{15}\text{ClO}$ is produced, which crystallises in small, colourless needles melting at

140°. When heated at its melting point, hydrogen chloride is given off, and a ketone, $C_{16}H_{14}O$, is formed, which crystallises from alcohol and melts at 53—54°. This ketone is isomeric with the one produced in the condensation with potassium hydroxide, and if in the first case benzyl styryl ketone is produced, this substance must be stilbyl methyl ketone, or *vice versa*, or it may be a stereoisomeride. Further experiments must decide this point.

If sulphuric acid is used for effecting the condensation, the product is a *hydrocarbon* of the formula $C_{27}H_{24}$, probably formed in a similar manner to mesitylene from acetone; it crystallises from alcohol in colourless leaflets melting at 120°. A. W. C.

Furfurobenzidine. By HUGO SCHIFF (*Ber.*, 1897, 30, 2302—2303).—A claim for priority.

Hydroxybenzylideneindanedione. By STANISLAUS VON KOSTANECKI and L. LACZKOWSKI (*Ber.*, 1897, 30, 2138—2144).—*Ortho-hydroxybenzylideneindanedione*, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:CH \cdot C_6H_4 \cdot OH$, obtained by heating indanedione with salicylaldehyde at 100°, crystallises in rosette-shaped groups of orange-red prisms, which have a violet surface lustre and decompose at 196°. It forms a yellow solution in concentrated sulphuric acid, and is readily decomposed by alkalis. Acetic anhydride converts it into the *acetyl* derivative, which crystallises in rosette-shaped groups of yellow needles melting at 124—125°. *Orthoethoxybenzylideneindanedione*,



can only be prepared by the action of ethylsalicylaldehyde on indanedione. It forms small, yellow crystals melting at 135° and yields a red solution with sulphuric acid. *Metahydroxybenzylideneindanedione* crystallises in yellow plates melting at 222°, and its *acetyl* derivative crystallises in yellowish needles melting at 140°. *Metethoxybenzylideneindanedione* crystallises in yellowish plates melting at 131—132°. *Para-hydroxybenzylideneindanedione* separates from acetic acid in lustrous, orange-yellow needles melting at 239°, and its *acetyl* derivative also forms yellow needles which melt at 162°, whilst *parethoxybenzylideneindanedione* crystallises in matted, yellow needles and melts at 139°.

Furfurylideneindanedione, $C_6H_4:(CO)_2:C:CH \cdot C_4H_3O$, obtained by the condensation of furfuraldehyde with indanedione, crystallises in lustrous, greenish needles melting at 203°.

Cinnamylideneindanedione, $C_6H_4:(CO)_2:C:CH \cdot CH:CHPh$, is prepared from cinnamaldehyde, and crystallises in long, orange-coloured needles melting at 150—151°.

When indanedione is heated at 120—125°, the anhydrodi-indanedione which is produced (Wislicenus and Kötze, *Abstr.*, 1889, 1067) is accompanied by tribenzoylenebenzene, $C_{27}H_{12}O_3$, which was first obtained by Gabriel and Michael (*Abstr.*, 1878, 229). A. H.

Action of Methylc Iodide on Aqueous Solutions of Crystal-Violet, Malachite-Green and Methylene-Blue; Hydrolysis of these Colouring Matters. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [iii], 15, 1299—1313).—When an aqueous solution of

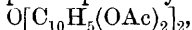
crystal-violet, $\text{CCl}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$ is mixed with methylic iodide, lustrous, long needles of the corresponding iodine compound gradually separate, and aniline-green and the compound $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2\text{I})_3 \cdot \text{OH} + 3\text{H}_2\text{O}$ are formed in smaller quantity at the same time, the production of aniline-green being greater the higher the temperature. In dilute solutions (1 part of crystal violet in 800 parts of water), aniline-green is not formed. Detailed investigation of the reaction leads to the following conclusions. In dilute aqueous solutions, methylic iodide acts on the compound $\text{CCl}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$ with formation of the corresponding iodine derivative and methylic chloride. Part of the methylic iodide is hydrolysed and the hydrogen iodide also interacts with the crystal-violet, forming a further quantity of the iodine compound. Part of the violet is also decomposed by water with liberation of hydrochloric acid and formation of the corresponding carbinol, and the latter combines with methylic iodide, yielding the compound $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2\text{I})_3 \cdot \text{OH}$; the methylic chloride formed in the reaction is also partially hydrolysed, and the liberated acid retards the action. The formation of the methiodide is subsequent to the formation of the carbinol.

A dilute aqueous solution of malachite-green, under similar conditions, yields the compound $\text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2\text{I}$ in lustrous crystals, together with methiodides, the reaction being similar to that with crystal-violet. Methylene-blue behaves similarly, and it would seem that the dialkyltri-amido-derivatives of triphenylcarbinol unite directly with methylic iodide, which converts them into iodammoniums at the ordinary temperature, even in presence of large quantities of water. The colouring matters in aqueous solution are partly hydrolysed, and when combination with methylic iodide suppresses the basic function, the acid remains free. The author points out that the occurrence of hydrolysis furnishes no definite evidence as to the constitution of the compounds (compare Abstr., 1896, i, 376, 377).

C. H. B.

Di- β -naphthaquinone Oxide. By K. HERMANN WICHELHAUS (*Ber.*, 1897, 30, 2199—2203).—*Di- β -naphthaquinone oxide*, $\text{O}(\text{C}_{10}\text{H}_5\text{O}_2)_2$, which is readily prepared from β -naphthaquinone by oxidation with ferric chloride, crystallises from acetic acid or acetone in slender, orange-yellow needles which melt at 245° , and yields two hydrates on treatment with water, one of which, $\text{C}_{20}\text{H}_{10}\text{O}_5 + 2\text{H}_2\text{O}$, is red, the other, $\text{C}_{20}\text{H}_{10}\text{O}_5 + 5\text{H}_2\text{O}$, black; the latter is converted into the former on heating it to 110 — 120° .

On reducing the freshly precipitated oxide with stannous chloride and hydrochloric acid, it is converted into an unstable compound, which yields an *acetyl* compound probably of the constitution



melting at 164 — 165° ; by the action of sulphurous acid a *substance*, $\text{C}_{20}\text{H}_{14}\text{O}_5$, melting at 138° is obtained.

The *oxime* of *di- β -naphthaquinone oxide* is only slightly soluble in water, the *phenylhydrazone* is brick-red, melts at 264° , and colours wool and silk yellow; the oxide further forms compounds with aniline, dimethylaniline, quinoline and resorcinol, the analyses of which show the correctness of the above formula.

J. F. T.

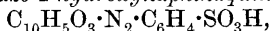
Azoquinones. By FRIEDRICH KEHRMANN and M. GOLDENBERG (*Ber.*, 1897, **30**, 2125—2130).—2-Hydroxy- α -naphthaquinone readily reacts with diazo-salts to form azo-compounds in which the nitrogen atom occupies the position 3 in the naphthalene ring, and which are converted by reduction into 2-hydroxy-3-amido- α -naphthaquinone and the base corresponding with the diazo-salt employed. These hydroxyazoquinones are brick-red to dark-red in colour and yield crystalline salts with bases, the ammonium salts being specially characteristic. 3-Benzeneazo-2-hydroxynaphthaquinone,



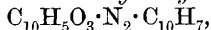
crystallises in fascicular groups of needles melting and decomposing at 225—226°. The ammonium salt forms violet-brown, lustrous needles which decompose at 215—217°. The silver salt is a black powder. The oxime, $\text{OH} \cdot \text{C}_{10}\text{H}_4\text{O}(\text{NOH}) \cdot \text{N}_2 \cdot \text{Ph}$, is a sulphur-yellow, crystalline powder which forms a blood-red solution in sulphuric acid.

3-Orthotolueneazo-2-hydroxynaphthaquinone, $\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$, crystallises in garnet-red needles, which have a blue, metallic lustre and melt at 205°. The ammonium salt forms dark-red, lustrous needles decomposing at 198°, and the oxime is an orange-yellow, crystalline powder decomposing at 210—212°. 3-Paratolueneazo-2-hydroxynaphthaquinone crystallises in light red needles which melt and decompose at 205°; whilst the oxime is a brownish-yellow, crystalline powder which melts and decomposes at 176—178°. 3-Orthonitrobenzeneazo-2-hydroxynaphthaquinone crystallises in orange-yellow needles which melt and decompose at 255—257°. 3-Paranitrobenzeneazo-2-hydroxynaphthaquinone forms orange coloured plates decomposing at 260—261°.

3-Parasulphobenzeneazo-2-hydroxynaphthaquinone,



forms a sodium salt which crystallises in yellowish-red plates. Parasulphonaphthaleneazohydroxynaphthaquinone, $\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6\text{SO}_3\text{H}$, yields a sodium salt which crystallises in small, dark-brown, sparingly soluble needles. β -Naphthaleneazohydroxynaphthaquinone,



crystallises in garnet-red needles decomposing at 247—248°. A. H.

Methylamide and Dimethylamide of Naphthalene- β -sulphonic Acid. By L. T. C. SCHEY (*Rec. Trav. Chim.*, 1897, **16**, 181—183).—The requisite quantity of standard potassium hydroxide solution is added to 3 grams of methylamine hydrochloride dissolved in a small quantity of water, ether is run in and then 5 grams of naphthalene- β -sulphonic chloride; after vigorously shaking, half the quantity of potash solution previously used, and then $2\frac{1}{2}$ grams of the chloride are added, this process being repeated until 10 grams of chloride have been added to 3 grams of methylamine hydrochloride. The white deposit which separates together with the residue left on evaporating the ethereal solution is recrystallised from alcohol, when the methylamide is obtained in a crystalline form melting at 107°. It is sparingly soluble in cold water, ether, or light petroleum, more readily in hot water, and dissolves with extreme ease in absolute alcohol, benzene or chloroform.

Naphthalene- β -sulphondimethylamide, is much more readily soluble in

ether, from which it crystallises in plates melting at 96° . It is not soluble in cold water, but dissolves with great ease in chloroform or benzene. J. J. S.

Constituents of Oil of Roses and Allied Ethereal Oils. By HUGO ERDMANN (*J. pr. Chem.*, 1897, [ii], 56, 1—47) (with ERNST ERDMANN).—*Pure rhodinol*, $C_{10}H_{17}\cdot OH$, was prepared from silver rhodinylic phthalate (see below), itself obtained from commercial geraniol, by treating it with sodium chloride, hydrolysing the resulting sodium salt with alkali, and distilling over the rhodinol with steam; if it is prepared by the hydrolysis of the diphenylurethane, it is difficult to free it from diphenylamine. It boils at 110.5 — 111° under 16 mm. pressure, and can be boiled under atmospheric pressure, but then undergoes a certain amount of decomposition; it has sp. gr. $= 0.8812$ at $16^{\circ}/4^{\circ}$; and it has a most pleasant odour of roses. If a drop is diluted with 5 c.c. of alcohol in a porcelain basin and 10 drops of strong sulphuric acid added, the latter becomes orange-yellow; when the basin is gently swayed, this colour changes to reddish-violet at the surface of separation between the two liquids, and disappears entirely as the liquids mix completely. This may be used as a qualitative test for rhodinol, although both linalool and citronellol give somewhat similar colorations.

Characteristic Derivatives of Rhodinol (with P. HUTH).—Diphenylcarbamic chloride is best obtained by dissolving diphenylamine (100 grams) in chloroform (300 c.c.), and passing in excess of carbonic chloride (40—50 grams). In this way, half of the diphenylamine is recovered as the hydrochloride; by adding pyridine (50 grams), a complete conversion is obtained, pyridine hydrochloride being formed; the carbonic chloride (60 grams) is in this case passed in at 0° . Rhodinylic diphenylurethane, $NPh_2\cdot COOC_{10}H_{17}$ (*Abstr.*, 1896, i, 198) was prepared from crude rhodinol obtained by the acetate method from genuine geranium oil produced at Grasse, in the south of France; it was heated (50 c.c.) with diphenylcarbamic chloride (75 grams) and pyridine (35 c.c.) for 5 hours at 100° , the product being washed with dilute acid, alkaline carbonate and water, freed from impurities by distilling these over with steam, and finally crystallised from alcohol. It melts at 82.2° , and forms a *tetrabromide*, melting when not quite pure at 129 — 132° , but it also readily takes up 6 other atoms of bromine by substitution, after which it very readily decomposes, yielding hexabromodiphenylamine as one of the products. *Rhodinylic benzoate*, obtained by gradually adding benzoic chloride (20 c.c.) to a mixture of rhodinol (30 c.c.) and pyridine (25 c.c.) kept at 0° , is a colourless oil, and boils at 194 — 195° under 12 mm. pressure. *Rhodinylic hydrogen phthalate*, $COOH\cdot C_6H_4\cdot COOC_{10}H_{17}$, is obtained by heating rhodinol (10 c.c.) with finely powdered phthalic anhydride (8.6 grams) in the water bath, with constant shaking until solution is just complete, and distilling over impurities with steam; it is a colourless syrup with acid properties, and inflames the mucous membrane when brought in contact with it. The *silver* salt provokes sneezing when inhaled; it melts at 133° ; it can be purified by dissolving it in its own weight of benzene and precipitating it with

warm methylic alcohol; it reacts with methylic and ethylic iodides and benzylic chloride in benzene solution, forming *methylic*, *ethylic*, and *benzylic* salts, which are oils that decompose when distilled.

Many of the usual analogies do not hold in the case of rhodinol. It does not react readily with carbamic chlorides other than the diphenyl one; with *paraditolyl*- (melting at 103°) and *α -dinaphthyl-carbamic chlorides* no compound could be obtained, and *phenylbenzylcarbamic chloride* gave a liquid compound of doubtful purity; *β -dinaphthylcarbamic chloride* melting at 151° , does, however, yield a crystallised *rhodinylic urethane* which melts at 105 — 107° . Further, diphenylcarbamic chloride itself does not react with other alcohols more or less similar to rhodinol; with linalool, terpineol and amylene hydrate, for example, no compound is formed; citronellol, however, forms a liquid diphenylurethane, which does not solidify at 0° . Again, although ethylic bromide reacts but slowly and incompletely with silver rhodinylic phthalate, benzylic chloride reacts quite readily; and although benzylic chloride reacts, paranitrobenzylic chloride does not. Lastly, no other anhydrides of dibasic acids, not even tetrachloro- and tetrabromophthalic anhydrides, react with rhodinol as phthalic anhydride does, yielding a product from which rhodinol can easily be recovered.

Occurrence and Detection of Rhodinol in Ethereal Oils (with P. HUTN). —The possible presence of rhodinol is first recognised by the sulphuric acid test. The oil (1 gram) is then heated in a test-tube with diphenylcarbamic chloride (1.5 grams) and pyridine (1.35 grams) for 2 hours at 100° , and the product is distilled with steam until a litre of distillate has collected, diphenylamine, derived from unchanged carbamic chloride, passing over. The residue, which solidifies on cooling, is recrystallised from 30 times its weight of alcohol; the yield of solid crystalline product is much reduced if citronellol is present, as this forms a liquid urethane. In this way, samples of oil of roses from Turkey and Germany were examined; of geranium oil from France, Bourbon (Réunion) and Syria; oil of ginger-grass; of citronella; of palmarosa from Turkey, and of neroli, both "bigarade" and from Portugal. The results varied extremely. Turkish oil of roses gave the greatest, the samples of oil of neroli the smallest, yield of crystalline diphenylurethane. Geraniol can be freed by Monnet's method from non-alcoholic constituents; it is heated with acetic anhydride at 140° for 8 hours, the acetates are purified and then hydrolysed with alcoholic potash, and the oil thus obtained is distilled under diminished pressure. Rhodinol is the chief constituent; a sample from Schimmel of Leipzig was found to owe its less pleasant odour to the presence of chlorine compounds, so that commercial geraniol stands in much the same relation to pure rhodinol as does synthetical benzaldehyde to oil of bitter almonds. Commercial rhodinol, from the Societe Chimique des Usines du Rhône at Lyon yielded a rhodinol identical with that obtained from geraniol; the heat of combustion is 3026 Cal. in both cases. Mixed with the rhodinol is citronellol, $C_{10}H_{19}\cdot OH$, which was isolated and converted into derivatives. *Citronellylic hydrogen phthalate* resembles the rhodinylic compound but is more stable; the *silver* salt melts at 120 — 124° ; the liquid *methylic* salt was also prepared, and so was liquid *citronellylic diphenylurethane*.

Preparation of Menthyllic Carbonate.—Menthol (30 grams) is dissolved in chloroform (30 c.c.), pyridine (25 c.c.) is added, the whole cooled by a freezing mixture, and 55 grams of a chloroform solution of carbonic chloride (containing 10 grams) slowly added; after being left for a day in the cold, the product is distilled with steam, and the solidified residue washed with hot water and recrystallised from alcohol. Menthyllic carbonate melts at 105°.

Remarks.—Of these the most important is to the effect that the name *geraniol* must be abandoned, the substance being identical with *rhodinol*.

C. F. B.

Oil of Cloves. By ERNST ERDMANN (*J. pr. Chem.*, 1897, 56, 143—156).—When oil of cloves is treated with an aqueous potash solution, a residue containing oxygen is left undissolved; this the author calls “échappés.” It has no constant boiling point, and its sp. gr. is lower than that of oil of cloves; when treated with alcoholic potash, there is a rise in temperature, and on extracting with ether caryophyllene is obtained. The residual alkaline liquid contains eugenol and acetic acid.

When “échappés” is distilled under a pressure of 12 mm. at a temperature of 142°, a solid substance collects in the receiver; this is found to be acetyleneugenol, thus accounting for the fact that the portion of oil of cloves insoluble in dilute potash solution contains oxygen.

Acetyleneugenol, prepared by treating pure eugenol with acetic anhydride, boils at 145—146° (8·5 mm.), has a sp. gr. = 1·0842 at 15°, is volatile with steam, and crystallises from alcohol in large, rhombic plates melting at 29°.

Thom's method (*Verhandl. der Gesellsch. Deutsch. Natur. f. w. Aerzte*, 1891, 184) for estimating the value of oil of cloves, and which presupposes the existence of free eugenol in the oil, gives numbers which are too low, because the acetyleneugenol is only partially estimated when this method is employed; if, however, the oil of cloves be first saponified, the true value can be obtained.

When oil of cloves is treated with alcoholic potash, and the free alkali titrated with normal hydrochloric acid, using litmus as indicator, it is found that a greater amount of alkali has been used up than is accounted for by the presence of acetyleneugenol; this is because salicylic acid is present in small amount, probably combined with eugenol as acetylsalicylic acid.

The author has further proved the presence of furfuraldehyde in oil of cloves.

A. W. C.

Ethereal Oil of Angostura-bark. By HEINRICH BECKURTS and JULIUS TROEGER (*Arch. Pharm.*, 1897, 235, 518—535).—This ethereal oil is obtained from the dark-brown oily liquid left after the alkaloids have been removed from the ethereal extract of the bark by shaking it with dilute sulphuric acid. The residue left is distilled with steam and the portion of the distillate insoluble in water is dried by means of anhydrous sodium sulphate; it is a yellowish oil which becomes darker after a time, and has an aromatic taste and odour; it is easily soluble in the ordinary organic solvents. Its physical properties agree with those of Schimmel and Co.'s preparation, and according to this firm the bark yields 1·5 per cent. of pure oil. The crude oil has

a rotatory power in a Wild's polaristrobometer = -50° (100 mm. tube); sp. gr. = 0.941 at 20° ; refractive index $n_D = 1.50624$. The analytical results obtained with different specimens were not concordant; this is also the case with oils from cubebs, preparations from old plants containing cubeb camphor, whilst those from younger plants consist essentially of terpene.

Attempts to isolate the substances contained in the oil, by fractional distillation both at the ordinary pressure and under diminished pressure, failed to give satisfactory results, owing to elimination of water arising from decomposition of the alcoholic constituent of the oil. In one distillation at the ordinary pressure, however, analysis of the fraction boiling at $260\text{--}270^\circ$, of which the major portion distilled at $264\text{--}265^\circ$, showed a composition corresponding with galipene alcohol, $C_{15}H_{26}O$, and on heating with acetic anhydride this fraction gave galipene, $C_{15}H_{24}$. *Galipene alcohol*, which is soluble in the ordinary solvents, does not possess the characteristic odour of the crude oil, and is optically inactive; sp. gr. = 0.9270 at 20° ; refractive index $n_D = 1.50624$. By the action of phosphorus pentachloride, a clear oil of pleasant odour and containing chlorine is obtained.

Galipene, obtained by the action of acetic anhydride on the alcohol or on the fractions boiling at $250\text{--}280^\circ$, is a yellowish oil which boils between 256° and 260° , the major portion distilling at $258\text{--}259^\circ$. It is more mobile than the crude oil, and has a fainter odour. It is soluble in the ordinary solvents; sp. gr. = 0.9110 at 20° ; rotatory power = 18° (100 mm. tube); refractive index $n_D = 1.50374$. The *hydrochloride*, $C_{15}H_{24}.2HCl$, is obtained by the action of hydrogen chloride dissolved in acetic acid; this solution does not at first mix with the terpene, but there is a dark-red zone of demarcation; the upper portion then gradually becomes violet and the lower red, and finally, after several days, mixture may be effected by shaking. The hydrochloride crystallises in transparent prisms and melts at $114\text{--}115^\circ$; the *hydrobromide* crystallises in lustrous, prismatic needles and melts at 123° .

The fraction of the crude oil boiling at $260\text{--}265^\circ$ was in one instance green; analysis indicated the composition of a terpene, and the hydrobromide prepared from it melted at 124° .

When the residue left after distillation at 280° under the ordinary pressure, or at 200° under 92 mm. pressure, is shaken with alcohol, it leaves a dirty green to yellowish-white, amorphous substance which is insoluble in cold alcohol, easily soluble in ethylic acetate, ether, and light petroleum, and partly soluble in acetic acid. It does not show a constant melting point, decomposes at $110\text{--}120^\circ$, becoming brown or black, and then melts at $130\text{--}140^\circ$. From the analysis, it appears to be a substance containing oxygen and formed from the alcohol by distillation.

Since the crude oil is levorotatory, the alcohol inactive, and the terpene dextrorotatory, it is probable that in the isolation of the terpene from the crude oil an inversion is effected, and that the terpene contained in the oil has a rotatory power different from that of the terpene obtained from it by means of acetic anhydride.

E. W. W.

Sinigrin, Sinalbin, Sinapin, Sinapic Acid. By JOHANNES GADAMER (*Ber.*, 1897, 30, 2322—2327; 2327—2328; 2328—2330;

2330—2334).—The main facts in these papers have already appeared (Abstr., 1897, i, 254 and 360).

Glucosides contained in the Root of *Helleborus niger*: Helleborein and Helleborin. By K. THAETER (*Arch. Pharm.*, 1897, 235, 414—424).—Of these glucosides, the former is easily soluble in water, but insoluble in ether, and the latter is insoluble in water but soluble in ether.

Helleborein is obtained from the aqueous extract by preparing from it the tannin compound of the glucoside and treating this with lead hydroxide, which liberates the glucoside; this is purified by repeated solution in absolute alcohol, and precipitation by ether. From a solution in 96 per cent. alcohol, only a yellow, amorphous, very hygroscopic mass separates, but from absolute alcohol fine needles are obtained which, although not as hygroscopic as Husemann and Marmé's preparation, have the same physical properties. The author's analysis, however, indicates an empirical formula, $C_{37}H_{56}O_{18}$, and the analysis of the blue product, which Husemann and Marmé named helleboretin, corresponds with the formula $C_{19}H_{30}O_5$; this can be obtained from helleborein by the action of dilute hydrochloric or sulphuric acid, dextrose and acetic acid being also formed. The acetic acid is not derived from a secondary action of the mineral acid on helleboretin, for the latter is not affected by dilute sulphuric acid. By fusion with alkalis, helleboretin yields formic acid and a substance which is soluble in alcohol and ether, but gives no colour reaction with ferric chloride. By oxidising helleboretin with chromic acid mixture, and subsequently distilling with steam, a distillate containing formic acid, and probably higher homologues of this acid, is obtained; a white substance insoluble in water and acids, but easily soluble in alcohol, is left in the retort; this gives no coloration with ferric chloride. With concentrated nitric acid, helleboretin gives an intensely violet solution which deposits violet flakes on pouring it into water and allowing it to stand. Neither dilute nor concentrated nitric acid gives any coloration with helleborein, and no helleboretin is formed.

Husemann and Marmé's method of preparing helleborin did not prove successful, but the author obtained it from the ethereal extract by treating it with light petroleum to remove the fatty compounds, and then with acetone, which dissolves tarry and colouring matters. The residual helleborin can be purified by crystallisation from a mixture of ether and alcohol, and is then pure white; in its physical properties it agrees with those of Husemann and Marmé's preparation, and gives the characteristic violet-red coloration with concentrated sulphuric acid, but the author's analysis indicates an empirical formula $C_6H_{10}O$.
E. W. W.

Substances contained in the Root of *Baptisia tinctoria* R.Br. ψ -Baptisin. By K. GORTER (*Arch. Pharm.*, 1897, 235, 494—503. Compare Abstr., 1897, i, 625).— ψ -Baptisin, $C_{27}H_{30}O_{14}$, is obtained from Merck's baptisin by crystallisation first from dilute alcohol, then from hot water, and finally from dilute spirit. It crystallises in colourless needles, is tasteless, and contains neither nitrogen nor

water. It melts at $247-248^{\circ}$, is soluble in boiling water, alcohol of 50 per cent. or acetone, very soluble in methylic alcohol, but insoluble in cold water, ether, acetone, benzene, chloroform, and dilute spirit, the specific rotatory power $[\alpha]_D = -101^{\circ} 40'$. With sulphuric acid, it gives a yellowish-brown coloration passing into orange-red; with Erdmann's reagent a very fugitive green coloration passing through reddish-violet to reddish-brown, and becoming green on addition of water; with a solution of iodic acid in concentrated sulphuric acid, it gives successively violet, red, olive-green, and yellow colorations. Millon's reagent produces a pale red coloration on boiling, and ferric chloride colours a solution in methylic alcohol yellowish-brown. It does not reduce Fehling's solution even on boiling with it for a short time, but reduction takes place with ease after it has been treated with sulphuric acid. From dilute alcohol, it crystallises with $7\frac{1}{2}\text{H}_2\text{O}$ or $4\text{H}_2\text{O}$, and, after drying over sulphuric acid, it contains $1\frac{1}{2}\text{H}_2\text{O}$, which may be driven off at $125-130^{\circ}$, the substance becoming slightly yellow. A solution of ψ -baptisin in methylic alcohol after a time deposits crystals of an additive product, $\text{C}_{27}\text{H}_{30}\text{O}_{14}\cdot\text{MeOH} + 1\frac{1}{2}\text{H}_2\text{O}$, which is insoluble in water, methylic alcohol, chloroform, and ethylic acetate, and loses both methylic alcohol and water if kept over sulphuric acid.

By boiling ψ -baptisin with dilute sulphuric acid, ψ -baptigenin, $\text{C}_{15}\text{H}_{10}\text{O}_5$, glucose, and rhamnose are formed. The first is a white, crystalline compound, does not melt below 270° , is insoluble in cold water, acetone, methylic and ethylic alcohols, but soluble in hot acetone and hot methylic alcohol. By mixing with 5 per cent. sodium hydroxide solution, a fine, crystalline, sodium compound is obtained, which is soluble in water but can be salted out by sodium chloride. ψ -Baptigenin dissolves in ammonia on slightly warming, forming a solution which gives a precipitate with lead acetate, but does not reduce ammoniacal silver nitrate solution. Baptigenetin and formic acid are produced on boiling ψ -baptigenin with 5 per cent. sodium hydroxide solution.

Acetyl- ψ -baptigenin, $\text{C}_{15}\text{H}_9\text{O}_5\text{Ac}$, melts at 173° , is insoluble in cold water, alcohol of 95 per cent., and light petroleum, but easily soluble in ethylic acetate, benzene, and acetone. On boiling with sodium hydroxide solution, baptigenetin is formed, but under certain conditions not yet determined, not baptigenetin but a substance which is probably *methylbaptigenetin* is obtained; the latter melts at $129-130^{\circ}$, crystallises in thin needles, and in alcoholic solution gives a red coloration with ferric chloride solution. E. W. W.

Filicic Acids. By RUDOLF BOEHM (*Chem. Centr.*, 1896, ii, 1036—1038; from *Arch. exp. Path. Pharm.*, **38**, 35—58).—In extracts of *Filix mas*. (male fern), the ethereal oil and filicic acid are not the only active ingredients. After mixing the extract with magnesia, and extracting with water, sulphuric acid added to the extract causes a voluminous precipitate; if this is dissolved in alcohol, crystals of *aspidin*, $\text{C}_{23}\text{H}_{32}\text{O}_7$, separate after a time; it has reducing properties, and contains a methoxyl group. It is a poison acting chiefly on the central nervous system. From the alcoholic mother liquor, another

crystalline compound, *albaspidin*, $C_{22}H_{28}O_7$, crystallises out. It contains no methoxyl group, and its physiological action resembles that of filicic acid.

From the mother liquor after the separation of this substance, a mono-basic acid *flavaspidic acid*, $C_{23}H_{28}O_8$, was separated; it crystallises in slender, golden-yellow prisms, and melts at $157-159^\circ$. Other substances obtained are *aspidinin*, crystallising in colourless, silky, rhombic tablets, and melting at 110° , and *aspidinol*, $C_{12}H_{16}O_4$, crystallising in thick, rhombic, bright yellow prisms, and melting at 143° ; the reactions of these are described.

By heating filicin (filicic acid) for 8 hours with 15 per cent. sodium hydroxide, phenol, phloroglucinol, and a new acid, *filicinic acid*, $C_{11}H_{14}O_4$, were obtained. The latter crystallises in cubes or octahedrons, melts at 215° , and on oxidation yields dimethylmalonic acid. The *methylic* salt melts at 208° , and the *ethylic* salt at 215° . W. D. H.

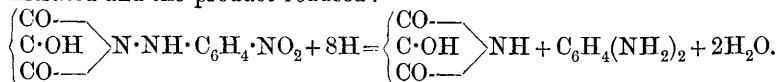
Cantharidin. By HANS MEYER (*Monatsh.*, 1897, 18, 393—410).—By neutralising a solution of cantharidin in water with caustic potash, using phenolphthalein as indicator, it is shown to contain one free carboxyl group. In order to determine the functions of the other two oxygen atoms, the cantharidin was treated with sodium methoxide and methylic iodide, when a dimethyl derivative was obtained; this was also produced on the etherification of cantharidin which had been exactly neutralised with caustic potash, but no monomethyl derivative was formed. The second methyl group must have replaced the hydrogen of a carboxyl or of a hydroxyl group. If the latter, then cantharidin should be capable of being acetylated, but this is not the case, and, moreover, if a hydroxyl group, then the fourth oxygen atom must belong to a ketone group, which is disproved by the facts given below. It appears probable, therefore, that the second methyl group is attached to carbonyl, which is explained by the presence of a lactone group, the latter being split at the moment of etherification. The hydroxyl group thus formed is attached to a tertiary carbon atom, since it does not react with acetic anhydride and sodium acetate, as it should do if it were a secondary one.

Homolka's observation (*Ber.*, 1885, 18, 987), that cantharidin must contain a ketone group, because cantharic acid, when treated with zinc chloride and dimethylaniline, condenses with formation of a green colouring matter, is not justifiable, especially as a similar reaction has been observed with many anhydrides, lactones, and dicarboxylic acids. Moreover, if cantharidin contains a ketone group, so must its dimethyl derivative, but it was found to be impossible to prepare a hydrazone from the latter.

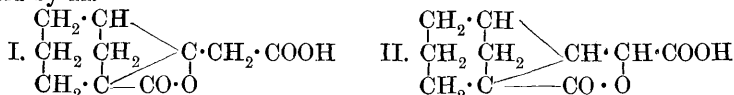
The substance formed by the action of hydroxylamine on cantharidin is an oxime, and by the action of phenylhydrazine an acid hydrazide is obtained and not a hydrazone as stated by Anderlini (*Abstr.*, 1890, 640), and Spiegel (*Abstr.*, 1892, 999; 1893, i, 40); this conclusion is supported by the fact that when cantharidin is heated

with alcoholic ammonia, an imide $\left\{ \begin{array}{l} \text{CO}- \\ \text{C}\cdot\text{OH} \\ \text{CO}- \end{array} \right\} \text{NH}$ is produced, in which

the hydrogen of the imide group can be replaced by methyl, yielding the same substance as is formed by the action of methylamine on cantharidin; and also when the phenylhydrazide of cantharidin is nitrated and the product reduced:—



From these considerations it appears probable that cantharidin is represented by the formulæ I, and the isomeric monobasic cantharic acid by II.



Dimethylcantharidin separates from chloroform in large, colourless, glistening crystals melting at 81—82°, can be distilled without decomposition under atmospheric pressure, when it boils at 296—298° (uncorr.), and is readily soluble in ether, alcohol, benzene, chloroform, pyridine, and boiling water.

Cantharidic acid phenylhydrazide, prepared by heating cantharidin with phenylhydrazine in molecular proportion at 200—220°, separates from acetone in small, glistening crystals melting at 236—238°. It gives Bulow's reaction for acid hydrazides and reduces Fehling's solution with liberation of nitrogen. A. W. C.

A Nitrogen Compound from the Buds of *Ricinus communis*. By ERNST SCHULZE (*Ber.*, 1897, 30, 2197—2198).—A well-defined crystalline compound containing nitrogen, *ricidine*, $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_3$, can be extracted from the dried buds of *Ricinus communis*, by treatment with 95 per cent. alcohol. It is sparingly soluble in water, but dissolves on warming, and separates again on cooling in small, colourless prisms melting at 193°, and differs from convicine in being soluble in hot alcohol, and not being precipitated by mercuric nitrate. The compound is present in the buds in considerable quantity. J. F. T.

Dipyridine Methyleniodide. By S. H. BAER and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1896, 18, 988—989).—The additive compound of pyridine and methylenic iodide is best prepared by the following method. The two are mixed in molecular proportion, an equal volume of alcohol is run in, and the whole heated for an hour on the water bath; after recrystallising the product from alcohol (50 per cent.), *dipyridine methyleniodide*, $(\text{C}_5\text{NH}_5)_2\text{CH}_2\text{I}_2$, is obtained in the form of slender, yellow needles decomposing at 220°. It is soluble in water, but insoluble in cold alcohol, ether, benzene, or chloroform.

Dipyridine ethylenbromide, $(\text{C}_5\text{NH}_5)_2\text{C}_2\text{H}_4\text{Br}_2$, crystallises in colourless plates melting and decomposing at 295°.

Monopyridine compounds with methylenic iodide and ethylenic bromide could not be obtained. J. J. S.

β -Toluoylpicolinic Acid and β -Tolyl Pyridyl Ketone. By ALEXANDER JUST (*Monatsh.*, 1897, 18, 452—459).— β -*Paratoluoylpicolinic acid*, $\text{C}_{14}\text{H}_{11}\text{NO}_3$, produced by the action of aluminium chloride on a solution of quinolinic anhydride in toluene, crystallises from

alcohol in microscopic, rhombic prisms melting at 166° , with evolution of carbonic anhydride; the air-dried crystals are anhydrous, and easily soluble in hot water and alcohol, but insoluble in benzene, ether, and chloroform. The *hydrochloride* crystallises in tufts of needles, the normal *silver* salt in microscopic crystals, and the *acid silver* salt in large, colourless, rhombic crystals.

β -*Paratolylpyridylorthoxazinone*, $C_{14}H_{10}N_2O_2$, obtained by the interaction of the above acid with hydroxylamine hydrochloride, forms colourless crystals melting at 217° with partial sublimation; it is insoluble in sodium carbonate.

1-*Phenyl-3-paratolylquinolinazone*, $C_{20}H_{15}N_3O$, obtained by the action of phenylhydrazine on toluoylpicolinic acid, crystallises in beautiful, yellow prisms melting at 247° ; it is soluble in benzene, sparingly so in water and ether, and insoluble in sodium carbonate solution. The *hydrochloride* and *platinochloride* are both yellow, crystalline substances.

β -*Paratolyl pyridyl ketone* is formed when toluoylpicolinic acid is heated at its melting point, carbonic anhydride being given off. It is very readily soluble in alcohol and benzene, but only sparingly in light petroleum and water; from dilute alcohol, it separates in colourless crystals melting at 78° .

The *hydrochloride* crystallises in needles, which are exceedingly soluble in water; the *platinochloride* in beautiful, yellow crystals; and the *oxime* in small, rhombic prisms melting at 167° . A. W. C.

Diacetyl-lutidine. By MAX SCHOLTZ (*Ber.*, 1897, 30, 2295—2299).—Acetylacetone (50 grams) and 40 per cent. formaldehyde (20 grams) readily condense in the presence of a few drops of piperidine to form *methylenediacetylacetone*, $CHAc_2 \cdot CH_2 \cdot CHAc_2$; this is a clear, syrupy liquid, and when saturated with ammonia at 0° , yields *diacetyldihydro-lutidine*, $CH_2 \left\langle \begin{smallmatrix} CAc: CMe \\ CAc: CMe \end{smallmatrix} \right\rangle NH$, which crystallises from alcohol in yellow needles melting at 198° , and dissolves in concentrated sulphuric acid and in dilute hydrochloric acid on warming. When oxidised with nitrous acid, according to Hantzsch's method, it yields *diacetyl-lutidine nitrate*, $C_{11}H_{13}NO_2 \cdot HNO_3$, melting and decomposing at 117° , and readily soluble in water, more sparingly in alcohol. The *base*, obtained by the action of potassium hydroxide on the nitrate, crystallises from ether in large, colourless plates melting at 72° . The *platinochloride*, $(C_{11}H_{13}NO_2)_2 \cdot H_2PtCl_6 + H_2O$, melts at 179° , and the *aurochloride* at 167° ; the *phenylhydrazone* is an oil, but the *di-phenylhydrazone hydrochloride*, $C_{11}H_{13}N(N \cdot NHPh)_2 \cdot HCl$, crystallises in needles. The *phenylhydrazone* of *diacetyl-lutidine nitrate* melts at 180° , and the corresponding *dihydrazone* at 232° . J. J. S.

β -Benzoylisonicotinic Acid. By MORIZ FREUND (*Monatsh.*, 1897, 18, 447—451).— β -*Benzoylisonicotinic acid*, $C_{13}H_9NO_3$, obtained by the action of aluminium chloride on a mixture of benzene and cinchomeronic anhydride, crystallises from water or dilute alcohol in colourless needles melting at 210 — 211° and gradually turning yellow on exposure to air. The *copper* salt crystallises in pale blue needles.

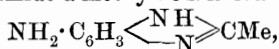
The free acid, when heated at 240° under a pressure of 40 mm., sublimes without decomposition, and this makes it appear probable that the carboxyl group is in the γ -position, a supposition which is proved by the fact that, on heating the acid with excess of lime, pyridine is produced. In a second experiment, using 2 parts of lime to 1 of the acid, no pyridine was obtained, but only a heavy yellow oil which consisted of β -phenyl pyridyl ketone, thus definitely proving the constitution of the original acid.

A. W. C.

Action of Hydrogen Peroxide on Tetrahydroquinoline and Tetrahydroisoquinoline. By EMIL MAASS and RICHARD WOLFFENSTEIN (*Ber.*, 1897, 30, 2189—2192).—In spite of many statements to the contrary, tetrahydroquinoline is not acted on by hydrogen peroxide, whilst tetrahydroisoquinoline alone yields *orthamidomethylphenylacetaldehyde*, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{COH}$; when pure, this forms white crystals melting at $76-77^{\circ}$; its *picrate* melts at 139° . The aldehyde, which readily polymerises on standing, yields tetrahydroisoquinoline on reduction with tin and hydrochloric acid. Sodium hydrogen sulphite readily reacts with it, forming *tetrahydroisoquinolinesulphonic acid*, which crystallises from alcohol and melts at $185-186^{\circ}$; the aldehyde yields a *benzoyl* compound which melts at $106-108^{\circ}$ and reduces Fehling's solution.

J. F. T.

Metamido- α -methylbenzimidazole, or Paramido- α -methylbenzimidazole. By ALFRED GALLINEK (*Ber.*, 1897, 30, 1909—1913. Compare Bamberger and Lorenzen, *Abstr.*, 1892, 631)—It was anticipated that metamido- α -methylbenzimidazole,



and paramido- α -methylbenzimidazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \text{H} \end{array} \text{CMe}$, would be formed by the reduction of orthonitracetylparaphenylenediamine and orthonitracetylmetaphenylenediamine respectively; these substances, however, yield the same anhydro-base, which is identical with Hobrecker's amidobenzimidazole (*Ber.*, 1872, 5, 923). This phenomenon appears to resemble the observations of von Pechmann (*Abstr.*, 1895, i, 347).

The base crystallises from water in aggregates of small, transparent plates containing $2\text{H}_2\text{O}$, and melts indefinitely at $55-80^{\circ}$; the solution is alkaline, and has a bitter taste. The *hydrochloride* is very readily soluble in water, and crystallises in silky needles; the *nitrate*, which is also readily soluble, forms long needles, and melts at 195° ; the *sulphate* crystallises in prisms, and melts at 274° , and the *picrate* at 207° . The *acetyl* derivative melts at 249° after crystallisation from water, but when alcohol is employed, the product melts at 324° . The silver derivative is white and amorphous.

Reduction of orthonitrodiaacetylmetaphenylenediamine gives rise to the same base. When diazotised, and combined with phenols, the substance yields colouring matters capable of directly dyeing cotton (compare *Abstr.*, 1894, i, 79, and 1896, i, 427).

M. O. F.

Reduction and Oxidation Products of $\alpha\mu$ -Dimethyloxazole and its Condensation with Acetaldehyde. By M. OESTERREICH

(*Ber.*, 1897, 30, 2254—2260. Compare Schuftan Abstr., 1896, i, 262).—A better yield of *αμ*-dimethyloxazole is obtained when acetamide and chloracetone are heated together for 10 hours at 120—125°. When an alcoholic solution of the base is reduced with sodium (four times the theoretical quantity), the chief product is *αμ*-dimethyloxalidine, $C_6H_{11}NO$. The mixture is treated with water and any unaltered oxazole is removed when the alcohol is distilled off; the residue when distilled on a sand bath yields the oxalidine, which after being dried with potash boils at 159°. It is an extremely strong base, with an odour resembling that of piperidine, and is readily soluble in alcohol or ether. Its *platinochloride* crystallises in yellowish-red needles readily soluble in water and decomposes at 180°; the *picrate* crystallises in lemon-yellow needles melting and decomposing at 103—104°. *αμ*-Dimethyloxazolidylphenylthiocarbamide, $C_{12}H_{16}N_2OS$, crystallises from its alcoholic solution in rhombic plates melting at 145°. The corresponding *phenylcarbamide*, $C_{12}H_{16}N_2O_2$, crystallises in needles melting at 225°. *Benzoyl-αμ*-dimethyloxazolidine, obtained by heating oxazolidine with benzoic chloride for 3—4 hours at 140°, crystallises in colourless plates melting at 105°. *μ*-Methyloxazole-*α*-carboxylic acid is prepared by adding dimethyloxazole to boiling potassium permanganate solution (4 per cent.) until the permanganate is decolorised. It is most readily purified by conversion into its silver salt, which may then be decomposed by hydrogen sulphide. It crystallises from water in long, colourless needles melting at 287—288°, and readily soluble in water, alcohol, or ether.

Methylpyriculine, C_4H_5N , is formed when dimethyloxazole (30 grams) and acetaldehyde (18 grams), are heated in a Pflugst's autoclave at 140—145° for 10 hours; when the product is distilled with alkali, a liquid is obtained which, on saturation with potash, yields a small quantity of an oil boiling at 156—157°. It is sparingly soluble in water, readily in ether or alcohol, and has an odour resembling that of pyridine. The *platinochloride*, $(C_4H_5N)_2H_3PtCl_6$, is a crystalline powder decomposing at 185°; the *aurochloride* crystallises in golden-yellow needles melting at 91—92°. The *picrate* melting and decomposing at 125°, the *phosphomolybdate*, *tannate*, and *mercuric chloride* derivatives are also described. J. J. S.

Nitro- and Amido-derivatives of Phenonaphthoxazone. By FRIEDRICH KEHRMANN and ERNST GAUHE (*Ber.*, 1897, 30, 2130—2138).—The authors have prepared three isomeric amidophenonaphthoxazones in order to ascertain the influence of the position of the amido-group on the colour and tinctorial properties of the phenonaphthoxazones. The amido-compounds are prepared by the reduction of the nitro-derivatives, formed by the condensation of nitro-derivatives of orthamidophenol with hydroxynaphthaquinone. The yield of nitrophenonaphthazoxazone is always small, an anilide being invariably formed. 2-Nitrophenonaphthoxazone, $C_{16}H_9O \begin{smallmatrix} N \\ \diagup \diagdown \\ O \end{smallmatrix} C_6H_3 \cdot NO_2$, prepared from 5-nitro-1:2-orthamidophenol, crystallises in yellowish-brown needles or plates melting at 246—247°. 2-Amidophenonaphthoxazone crystallises in violet-black needles, which have a

metallic lustre, melts at 255—256°, and forms yellow solutions in dilute mineral acids. The *anilide* from hydroxynaphthaquinone and 5-nitroorthamidophenol, $C_{10}H_5O_2 \cdot NH \cdot C_6H_5(NO_2) \cdot OH$, crystallises in long, lustrous, red needles, which decompose at about 240°; it is decomposed by boiling dilute aqueous alkalis, but not by the alkali carbonates. The *sodium* derivative crystallises in small, readily soluble, black needles. 3-Nitrophenonaphthoxazone crystallises in yellowish-brown needles which have a brassy lustre and melt at 253—254°; it yields fluorescent, yellow solutions in acetic acid and benzene, differing in this respect from its two isomerides. 3-Amidophenonaphthoxazone forms green needles, which have a strong metallic lustre, and decompose at 280° without melting; it yields fluorescent solutions when dissolved in the mineral acids or in a mixture of alcohol and benzene. The *anilide* crystallises in violet plates which decompose at about 270°.

A third nitro-compound of unknown constitution, obtained by the action of nitric acid on phenonaphthoxazone (Abstr., 1895, i, 245), melts at 234—235°, and not at 232° as previously stated, and is non-fluorescent; the corresponding *amido*-compound forms dark red, spherical aggregates of needles melting at 211—212°, the acid solutions of which are yellowish-green, and show no fluorescence. The nitro-amidophenol, which was thought by Friedländer and Zeitlin (Abstr., 1894, i, 184) to be most probably 6-nitroorthamidophenol, does not yield a phenonaphthoxazone with hydroxynaphthaquinone, but only forms an *anilide*, $C_{10}H_5O_2 \cdot NH \cdot C_6H_4(NO_2) \cdot OH$, which crystallises in light red plates.

Experiments which will be described in a separate communication have shown that the nitro-compound is in reality 6-nitroparamidophenol.

A. H.

Oxydichloropurine. By EMIL FISCHER and LORENZ ACH (*Ber.*, 1897, 30, 2208—2219).—When potassium urate is heated with phosphorus oxychloride at 160—170°, 8-oxy-2:6-dichloropurine,
$$\begin{array}{c} N:CCl \cdot C \cdot NH \\ | \\ CCl \cdot N \cdot C \cdot NH \end{array} > CO$$
, is formed, which closely resembles methyloxydichloropurine (Abstr., 1884, 996, 1308); it is best obtained pure by decomposition of the *ammonium* salt, which crystallises in faintly yellow plates. It decomposes above 350° without melting, and dissolves in about 120 parts of boiling alcohol or 1000 parts of boiling water. It is readily soluble in alkalis, and dissolves in concentrated sulphuric acid forming a solution from which it is precipitated by water, but when heated with concentrated hydrochloric acid at 120°, it is reconverted into uric acid. Methylic iodide converts the lead and potassium salts into 7:9-dimethyl-8-oxy-2:6-dichloropurine, and this reaction, therefore, furnishes a proof of the constitution of the compound. 7-Methyloxydichloropurine can be obtained by treating an alkaline solution of the potassium salt, at a low temperature, with methylic iodide in molecular proportion. 8-Oxydichloropurine is converted, by reduction with hydriodic acid and phosphonium iodide at 100°, into 8-oxyypurine,
$$\begin{array}{c} N:CH \cdot C \cdot NH \\ | \\ CH \cdot N \cdot C \cdot NH \end{array} > CO$$
, which is isomeric with hypoxanthine. It crystal-

lises in very slender, pliable needles, melts indefinitely at about 317° (corr.), and can be partially distilled at a higher temperature. It dissolves in alkalis and decomposes calcium carbonate, and also unites with mineral acids to form crystalline salts. The *hydriodide*, *hydrochloride*, and *hydrobromide* are all readily soluble, whilst the *nitrate* is only sparingly soluble; the *platinochloride* forms compact, yellow crystals, and the *aurochloride* slender, yellow plates. 8-Oxydichloropurine is converted by alcoholic ammonia at 150° into 6-amido-8-oxy-2-chloro-

purine,
$$\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CCl}:\text{N} \text{---} \text{C}\cdot\text{NH} \end{array} \text{>CO},$$
 which can be purified by conversion into

the barium salt, from which it is obtained in very slender, matted needles. It carbonises above 360° without melting, and is soluble both in acids and alkalis. The *barium* salt crystallises in long, colourless, slender needles. The *sulphate* forms fascicular groups of needles, and the *hydrochloride* also crystallises in needles. The base, by reduction with hydriodic acid, is converted into 6-amido-8-oxypurine,

$$\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CH}:\text{N} \text{---} \text{C}\cdot\text{NH} \end{array} \text{>CO},$$
 which crystallises in microscopic needles and

decomposes without melting when heated. The *sulphate* crystallises in oblique, four-sided plates and is sparingly soluble in water, whilst the *nitrate* is more readily soluble, and crystallises in slender needles. The base itself readily reduces ammoniacal silver oxide. When 8-oxydichloropurine is heated with aqueous ammonia, both the chlorine atoms are replaced by NH_2 , and 2:6-diamido-8-oxypurine,

$$\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{C}(\text{NH}_2):\text{N} \text{---} \text{C}\cdot\text{NH} \end{array} \text{>CO},$$
 is

formed; it crystallises with $1\text{H}_2\text{O}$ in colourless needles and decomposes above 380° . The *hydrochloride* crystallises in long, colourless needles, and is readily soluble, whilst both the *nitrate* and the *sulphate* are only sparingly soluble; the *platinochloride* forms yellowish-red plates.

6-Amido-8-oxypurine is converted by nitrous acid into 6:8-dioxy-

purine,
$$\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CH}:\text{N} \text{---} \text{C}\cdot\text{NH} \end{array} \text{>CO},$$
 which is isomeric with xanthine. It

crystallises with $1\text{H}_2\text{O}$ in long, narrow, lustrous plates which decompose above 400° . It readily dissolves in alkalis, and forms a *barium* salt which crystallises in slender, sparingly soluble needles. It is easily oxidised by concentrated nitric acid, and does not yield alloxan when treated with potassium chlorate and hydrochloric acid. Methyl iodide converts it into 1:7:9-trimethyl-6:8-dioxypurine (Abstr., 1897, i, 642).

A. H.

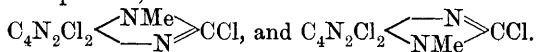
Trichloropurine. By EMIL FISCHER (*Ber.*, 1897, 30, 2220—2225).

—*Trichloropurine*,
$$\begin{array}{c} \text{N}:\text{CCl}\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CCl}:\text{N} \text{---} \text{C}\text{---} \text{N} \end{array} \text{>CCl},$$
 which is formed when 8-oxydi-

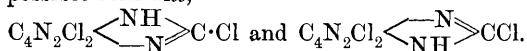
chloropurine is heated at $150\text{--}155^{\circ}$ with 70 parts of phosphorus oxychloride, crystallises with $5\text{H}_2\text{O}$ in large plates, which become anhydrous at 110° . The dry substance at $187\text{--}189^{\circ}$ (corr.) suddenly melts, and decomposes with evolution of gas. It dissolves in 70 parts of hot water, forming a strongly acid solution, and is not precipitated from solutions of its salts by acetic acid. The salts of the alkalis and alkaline earth metals are readily soluble, whilst the *zinc* salt is

insoluble. When it is heated with hydrochloric acid, trichloropurine is reconverted into 8-oxy-2:6-dichloropurine.

Methylic iodide converts it into a mixture of the two well-known methyltrichloropurines,



Since it yields these two isomeric methyl derivatives, the original trichloropurine is probably tautomeric, in this respect resembling certain of the amidines (von Pechmann, Abstr., 1897, i, 515), with which it is, moreover, analogous in constitution. Under these circumstances it has been impossible to assign to it with certainty either of the two possible formulæ,



It differs from its methyl derivatives in being strongly acid and in yielding up its chlorine atoms to bases in a different order. This circumstance has rendered it possible to synthesise xanthine, hypoxanthine, adenine, and guanine (compare following abstract).

A. H.

Synthesis of Xanthine, Hypoxanthine, Adenine, and Guanine. By EMIL FISCHER (*Ber.*, 1897, 30, 2226—2254. Compare the foregoing abstract, and Abstr., 1897, i, 267).—*Synthesis of Hypoxanthine.*—When trichloropurine is heated with normal aqueous potash, the chlorine atom in position 6 is removed, and 6-oxy-2:8-dichloro-

purine (dichlorhypoxanthine), $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \\ | \quad | \\ \text{CCl:N} - \text{C} - \text{N} \end{array} \text{CCl}$, is produced; this crystallises in colourless needles, becoming brown at above 350°, forms an acid solution in water, and yields crystalline salts with bases. Nitric acid slowly oxidises it, forming a solution which gives the murexide reaction. When reduced by means of hydriodic acid, it is converted into hypoxanthine; this dissolves in 69·5 parts of boiling water and in about 1400 parts at 19°. Since these numbers differ somewhat from those given by Strecker, and the other properties of the substance are not sufficiently characteristic for its certain identification, the dichlorohypoxanthine was converted by the action of methylic iodide into dimethyldichlorohypoxanthine, $\text{C}_7\text{Cl}_2\text{H}_6\text{N}_4\text{O}$; this crystallises in colourless needles and melts indefinitely between 252° and 263° (corr.). On reduction with hydriodic acid, it is converted into dimethylhypoxanthine, and the compound obtained in this way is identical in every respect with that prepared from adenine and from meat extract; it melts at 251—253° (corr.), and forms a characteristic compound with sodium iodide. The synthetical hypoxanthine is, therefore, identical with the natural product, and with that prepared from adenine.

Synthesis of Xanthine.—When trichloropurine is treated with alcoholic sodium ethoxide at the ordinary temperature, 6-ethoxy-2:8-dichloropurine, $\begin{array}{c} \text{N} \cdot \text{C}(\text{OEt}) \cdot \text{C} \cdot \text{NH} \\ | \quad | \\ \text{CCl:N} - \text{C} - \text{N} \end{array} \text{CCl}$, is formed; this crystallises in colourless, matted needles, and melts and decomposes at 203—204° (corr.). Hydriodic acid converts it into hypoxanthine. When the

trichloropurine is boiled with alcoholic sodium ethoxide, on the other hand, 2 : 6-diethoxy-8-chloropurine, $\begin{array}{c} \text{N}:\text{C}(\text{OEt})\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{C}(\text{OEt})\cdot\text{N}\cdot\text{C}-\text{N} \end{array} \gg \text{CCl}$, is formed.

This crystallises in colourless, slender, matted needles, and melts and decomposes at about 209° (corr.) ; when reduced with hydriodic acid, it yields xanthine, identical in all respects with the natural product. Diethoxychloropurine, when heated with hydrochloric acid, yields *chloroxanthine*, $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CO}\cdot\text{NH}\cdot\text{C}-\text{N} \end{array} \gg \text{CCl}$, which is a colourless, granular, crystalline powder and carbonises when heated ; its alkali salts are crystalline and soluble in water. Hydriodic acid converts it into xanthine. Methyl iodide converts chloroxanthine into chlorocaffeine, and from this caffeine and various other derivatives can be obtained, all identical with those from natural caffeine.

Synthesis of Adenine.—6-Amido-2 : 8-dichloropurine (dichloradenine), $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CCl}:\text{N}-\text{C}-\text{N} \end{array} \gg \text{CCl}$, obtained by the action of aqueous ammonia on trichloropurine, crystallises in stellate groups of microscopic needles, which become brown at above 300° . The alkali salts are crystalline and readily soluble in water. Hydriodic acid reduces it to adenine (6-amidopurine), $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CH}:\text{N}-\text{C}-\text{N} \end{array} \gg \text{CH}$, which is identical with the natural base ; when rapidly heated in a narrow tube, it suddenly melts and decomposes at $360-365^\circ$.

When amidodichloropurine is heated with hydrochloric acid at 100° , it loses one atom of chlorine and forms 6-amido-2-oxy-8-chloropurine, which has not itself been isolated, but is converted by hydriodic acid into the 6-amido-2-oxypurine described below. When, however, the reaction is carried out at $120-125^\circ$, 6-amido-2 : 8-dioxypurine, $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CO}\cdot\text{NH}-\text{C}\cdot\text{NH} \end{array} > \text{CO}$, is formed as a colourless, crystalline powder, which carbonises above 360° without melting, and is very sparingly soluble in hot water. The crystalline *barium* salt is almost insoluble in water ; the *hydrochloride* crystallises in compact prisms, and is decomposed by pure water ; the *sulphate* is very sparingly soluble. It differs from the isomeric 2-amido-6 : 8-dioxypurine in being much more readily soluble in warm ammonia, and in yielding no guanidine when it is oxidised with sodium chlorate and hydrochloric acid.

6-Amido-2-ethoxy-8-chloropurine, $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{C}(\text{OEt})\cdot\text{N}\cdot\text{C}-\text{N} \end{array} \gg \text{CCl}$, which is formed by the action of alcoholic sodium ethoxide on amidodichloropurine, crystallises in colourless needles, and does not melt, but softens between $275-280^\circ$ (corr.). Hydriodic acid converts it into 6-amido-2-oxypurine, $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CO}\cdot\text{NH}-\text{C}-\text{N} \end{array} \gg \text{CH}$, which is a white, amorphous mass, and carbonises when heated ; it is only very slightly soluble in hot water, and almost insoluble in alcohol ; its *sulphate* crystallises with $1\text{H}_2\text{O}$, and, like the other salts, is only sparingly soluble. 6-Amido-2-oxypurine closely resembles guanine, but does not yield

guanidine on oxidation, and can also be distinguished by the fact that guanine sulphate contains $2\text{H}_2\text{O}$. The constitution of adenine follows from that of 6-amidodioxypurine, but, as in the case of xanthine, it has so far been impossible to distinguish between the two possible tautomeric formulæ. Dichloradenine is converted by methylic iodide into a *methyl*dichloradenine, which melts and decomposes at 253° (corr.); this is more readily soluble both in water and acids than dichloradenine, and forms crystalline salts. Hydriodic acid reduces it to 9-methyladenine, identical with that prepared by Krüger (*Zeit. physiol. Chem.*, 18, 434) by the direct methylation of adenine.

Synthesis of Guanine.—When 6-oxy-2:8-dichloropurine is heated with alcoholic ammonia, it yields chloroguanine, which, by the action of hydriodic acid, is reduced to guanine; the latter is in every respect identical with the natural product. A. H.

Crystallised Xanthine and Guanine. By IAN HORBACZEWSKI (*Zeit. physiol. Chem.*, 1897, 23, 226—230).—Amorphous xanthine is dissolved in a little potash, the solution filtered, and diluted with distilled water at 60° so that 1 gram of xanthine is contained in 2 litres of the solution. The solution is then acidified with acetic acid, filtered rapidly, and allowed to cool slowly; after several days, the xanthine is deposited on the sides of the vessel in the form of colourless, glistening nodules which contain $1\text{H}_2\text{O}$. The crystals may also be obtained by using a somewhat stronger solution containing alcohol. They do not give up their water until heated to 125 — 130° .

A warm, dilute alkaline solution of guanine (1:2000) is mixed with about one-third of its volume of alcohol, acidified with acetic acid, and allowed to cool. The crystals of guanine which separate are anhydrous, and in appearance resemble creatinine-zinc chloride.

J. J. S.

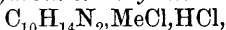
Derivatives of Theobromine. By WILLEM VAN DER SLOOTEN (*Arch. Pharm.*, 1897, 235, 469—490).—See Abstr., 1897, i, 382.

Oxidation of Ethyltheobromine by Potassium Chlorate and Hydrochloric Acid. By HERBERT POMMERHNE (*Arch. Pharm.*, 1897, 235, 490—494).—Ethyltheobromine, on oxidation with hydrochloric acid and potassium chlorate, yields methylamine, methylethylalloxan and *apoethyltheobromine*. The last forms tabular crystals and melts at 137 — 138° . E. W. W.

The Methiodides of Nicotine. By AMÉ PICTET and P. GENEQUAND (*Ber.*, 1897, 30, 2117—2125).—Nicotine dimethiodide, which was shortly described by Stahlschmidt (*Annalen*, 1854, 90, 222), crystallises in compact, light yellow prisms melting at 216° .

Nicotine methiodide, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{MeI}$, is obtained by mixing nicotine with methylic iodide, in molecular proportion, in methyl alcoholic solution; it is a light yellow, syrupy mass which cannot be made to crystallise. It is not decomposed by alkali carbonates, but when treated with silver oxide yields an alkaline solution, which probably contains the methohydroxide, and when evaporated with hydrochloric acid

leaves a residue of the *hydrochloride of nicotine methochloride*,

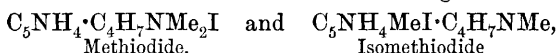


which is a colourless, deliquescent mass. The corresponding *platinochloride*, $C_{10}H_{14}N_2, MeHPtCl_6$, melts and decomposes at 266° . *Nicotine dihydriodide*, $C_{10}H_{14}N_2, 2HI$, formed by the direct action of hydriodic acid on the base, crystallises in long, colourless needles melting at 195° . When boiled with nicotine in alcoholic solution, it is converted into the *hydriodide*, which, like the corresponding methiodide, is a pale yellow, uncrystallisable mass. The monhydriodide is converted by methylic iodide into the *hydriodide of nicotine isomethiodide*, $C_{10}H_{14}N_2, HI, MeI$, which crystallises in colourless plates melting at 209° ; this compound is decomposed by sodium carbonate with formation of *nicotine iso-methiodide*, $C_{10}H_{14}N_2, MeI$, which crystallises in colourless plates melting at 164° . *Nicotine isomethochloride*, $C_{10}H_{14}N_2, MeCl$, forms a hygroscopic, radiating crystalline mass, and its *platinochloride* decomposes at $235\text{--}240^\circ$ without melting. Silver oxide converts the isomethiodide into the corresponding *hydroxide*, which could not, however, be isolated.

The formation of two isomeric quaternary iodides from nicotine proves that the two nitrogen atoms of this alkaloid are both tertiary. When the isohydroxide, corresponding with the isomethiodide, is oxidised by potassium permanganate, it is converted into trigonelline,



(the methylbetaine of nicotinic acid), and this reaction shows that the two methiodides have the following formulæ,



the nitrogen atom of the pyrrolidine ring being more basic than that of the pyridine ring.

A. H.

Alleged Conversion of Cinchonine into Cinchonidine. By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J. Trans.*, 1897, 58, 141).—The authors have subjected pure cinchonine to the action of a solution of potash in amylic alcohol, in the manner described by Koenigs and Husmann (*Abstr.*, 1896, i, 707), who claim to have converted 5 per cent. of the cinchonine into cinchonidine. They were not able to detect the slightest trace of cinchonidine in the product, and suggest that Koenigs and Husmann, in their experiments, employed cinchonine containing cinchonidine.

E. C. R.

Conversion of Cinchonine into Isomerides by Means of Acids. By ZDENKO H. SKRAUP (*Monatsh.*, 1897, 18, 411—417).—By the action of hydrochloric acid, cinchonine is partially converted into its isomerides, isocinchonine, and pseudocinchonine, and partially into the additive product.

No similar action is noticed in the case of cinchotine, but when the so-called neutral cinchotine hydrochloride is acted on by sulphuric acid, a portion of the base is converted into a *sulphonic acid*, which is easily separated from the unchanged substance by taking advantage of its solu-

bility in 50 per cent. alcohol containing excess of ammonia. The sulphonic acid crystallises in clusters of needles or leaflets containing varying amounts of water of crystallisation; it is only sparingly soluble in either water or alcohol, but is soluble in a mixture of the two liquids. It is coloured yellow at 220° and melts at 245—246° with decomposition and disengagement of gas. The base liberated by ammonia from this sulphonic acid agrees in melting point, appearance, and other properties with pure cinchotine.

Cinchonine contains a double linking, which is not present in cinchotine, and the author suggests that the resolution of the former into its isomerides may in some way be connected with this fact, for which assumption he hopes shortly to produce further evidence.

A. W. C.

Double Chlorides of Cinchonamine. By LÉON BOUTROUX and P. GENVRESSE (*Compt. rend.*, 1897, 125, 467—469).—Cinchonamine hydrochloride in aqueous solution readily combines with the chlorides of cadmium, zinc, or copper, forming double salts which contain 2 mols. of the organic base and 1 mol. of the metal. The cadmium compound crystallises readily in thin, elongated, rectangular plates, with truncated extremities very similar in appearance to the crystals of cinchonamine nitrate; when slowly formed, the crystals are thicker and shorter rhombic prisms with the face g^1 predominant. The zinc salt crystallises in silky, rhombic prisms, in which also the face g^1 is predominant, whilst the cupric salt forms brick-red crystals. All the crystals are anhydrous; the zinc and cadmium compounds are somewhat soluble in boiling water, but are quite insoluble in presence of hydrochloric acid; the cupric salt is dissociated by water, especially on heating.

Ferrous, magnesium, barium, and calcium chlorides seem to form no analogous compounds.

C. H. B.

Retamine. By J. BATTANDIER and TH. MALOSSE (*Compt. rend.*, 1897, 125, 450—451).—The molecular weight of retamine as determined from the boiling point of its solution in ethylic alcohol is 268·8; the analytical results agree very closely with the formula $C_{15}H_{26}N_2O$. It forms two hydrobromides, $C_{15}H_{26}N_2O \cdot HBr$ and $C_{15}H_{26}N_2O \cdot 2HBr$, and a hydriodide, $C_{15}H_{26}N_2O \cdot 2HI$, which crystallises readily. The sulphate crystallises from water with $4H_2O$, and from concentrated alcohol with $2H_2O$. Retamine salts of the type $R \cdot HBr$ are neutral to phenolphthalein, but salts of the type $R \cdot H_2SO_4$ are acid to this indicator. When the diacid salts are mixed with one equivalent of an alkali hydroxide, half the acid is removed, and the salts neutral to phenolphthalein are formed. Determinations of the molecular weight, by adding a known excess of acid to the retamine and then titrating back with an alkali hydroxide and phenolphthalein, give the number 250, which agrees with the formula $C_{15}H_{26}N_2O$.

C. H. B.

The Digitalis Alkaloids. By HEINRICH KILIANI (*Arch. Pharm.*, 1897, 235, 425—429).—In reply to Keller, the author states that digitalis leaves contain, in addition to digitoxin, another crystalline poison which is also soluble in chloroform, and gives a similar reaction with glacial acetic acid and sulphuric acid containing iron. This sub-

stance, which he names *digitophyllin*, $C_{32}H_{52}O_{10}$, is a glucoside, and crystallises from methylic alcohol in prisms or plates; it sinters at 224° , and melts and decomposes at $230-232^{\circ}$. It is not so easily attacked by dilute hydrochloric acid as digitoxin and is more insoluble, one part requiring more than 30 parts of methylic alcohol for solution. According to the author, digitophyllin is probably identical with the French "digitaline cristallisée." E. W. W.

Estimation of Alkyl Groups Attached to Nitrogen. By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1897, 18, 379—392. Compare Abstr., 1896, i, 68).—The authors now show that their method may be used for estimating alkyl groups attached to nitrogen, not only in the hydriodides, but in all salts and double salts of bases that are not explosive and that do not contain sulphur. A number of substances have been examined with results which do not in all cases agree with the observations of other investigators.

Pilocarpine cannot be considered as a dihydroxy-derivative of cytisine, because the latter contains no alkyl group attached to nitrogen, whereas pilocarpine contains an alkyl group (compare van der Moer, Abstr., 1890, i, 657). Pilocarpidine contains no alkyl group attached to nitrogen.

Morphine, apomorphine, scopolamine, and chelidonine each contain one methyl group.

Both the crystalline and amorphous varieties of bebirine contain one methyl and one methoxy-group, but no methyl connected to nitrogen.

Corydaline and bulbocarpine contain respectively four and one methyl groups (compare Dobie and Lander, Trans., 1892, 244 and 605, and Freund and Josephi, Abstr., 1894, i, 100).

Morphothebaine methiodide contains one methoxy- and two methyl groups, whilst stachhydrine and eserine each contain two methyl groups.

The authors point out that their method does apparently in some cases indicate more alkyl groups than are actually present, but such instances are of rare occurrence. A. W. C.

Intervention of Manganese in Oxidations produced by Laccase. By GABRIEL BERTRAND (*Compt. rend.*, 1897, 124, 1032—1035).—The ash of laccase, as the author has previously stated, contains a relatively large proportion of manganese; in one case, it amounted to as much as 2.5 per cent. of the ash. Fractional precipitation of the laccase gave products with different activities, and it was found that the activity increased with the quantities of manganese present. Attempts to obtain laccase free from manganese were unsuccessful, but a laccase extracted from lucerne contained very little of this element, and had very little oxidising power; on adding a small quantity of manganese sulphate, however, its oxidising power, as measured by means of quinol solution, became more than thirty times as great. Iron, aluminium, cerium, zinc, copper, calcium, magnesium, and potassium have no effect similar to that exerted by manganese. It seems probable that manganese, which exists in small quantities in living organisms, has important functions that have hitherto been unrecognised, probably because the proportion of the element usually present is so minute. C. H. B.

Chemical Behaviour of Diastase and Occurrence of an Araban in Ordinary Diastase. By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1897, 30, 2289—2295).—Finely ground malt is extracted first with 68 per cent. alcohol and then twice with 45 per cent. alcohol. On the addition of alcohol to the latter extract, the diastase is precipitated, the operation of solution in 45 per cent. alcohol and precipitation is repeated, and then the diastase is dissolved in water and salted out with magnesium sulphate; it is freed from sulphate by dialysis and then precipitated by alcohol and ether. The diastase thus obtained is soluble in water, gives no colour with iodine, and has a strong diastatic action. It gives all the reactions for albumin with the exception of the biuret reaction, and does not reduce Fehling's solution. Aqueous solutions yield a voluminous precipitate with potassium mercury iodide and dilute hydrochloric acid; the filtrate from this, on the addition of alcohol, gives a precipitate consisting of araban. This carbohydrate has no diastatic action, is strongly laevorotatory, and on hydrolysis yields arabinose which is dextrorotatory; ordinary diastase consists mainly of this carbohydrate. The other constituent is a proteid which is precipitated by Brücke's reagent; it gives the ordinary proteid reactions, but yields no precipitate with lead acetate. When freshly prepared, it dissolves in water, but after treatment with alcohol it becomes insoluble, whilst a mixture of the soluble and insoluble varieties is obtained by boiling the commercial diastase with dilute sulphuric acid. Both varieties, when hydrolysed with 20 per cent. hydrochloric acid yield ammonia, nitrogen bases, leucine, and tyrosine, but no arginine. The author comes to the conclusion that diastase is a proteid substance, and he thinks that enzymes form a sub-class of the proteids.

J. J. S.

Action of Halogens on Albumin. By F. GOWLAND HOPKINS (*Ber.*, 1897, 30, 1860—1862).—Chlorine and bromine react in the cold with a solution of egg-albumin which has been freed from globulin, yielding voluminous precipitates, and a similar reaction takes place with iodine at 40—50°; after well washing and dialysing, the products obtained leave no ash on incineration, but contain halogen. The chlorine and bromine derivatives dissolve readily in a 5 per cent. solution of sodium carbonate, the iodine derivative somewhat more slowly; and from these solutions, acetic acid precipitates derivatives which still contain halogen, and which yield constant results on analysis. After 48 hours' dialysis, the chlorine compound prepared in this way contained 3.50—3.67 per cent. of chlorine, the bromine derivative 3.84 per cent. of bromine, and the iodine compound 6.11 to 6.29 per cent. of iodine. These compounds are insoluble in alcohol, ether, or benzene, and give the xanthoprotein and biuret reactions, but produce no coloration with Millon's reagent, neither do they blacken lead acetate solution when boiled with it. From the original precipitates produced by the action of the halogens on albumin, alcohol is capable of extracting substances rich in halogen, which appear to have a definite composition; these are precipitated from alcoholic solution on the addition of ether, and are sparingly soluble in water. Like the first-mentioned compounds, they give the xantho-

protein and biuret reactions, but no coloration with Millon's reagent. All the substances prepared differ from Paal's halogen peptones (Abstr., 1892, 895; 1894, i, 559) in their insolubility in water, in their acidic properties, and in showing no tendency to dialyse when in solution.

F. G. H.

Preparation of Deuteroalbumose. By SIGMUND FRÄNKEL (*Monatsh.*, 1897, 18, 433—436).—Deuteroalbumose free from protalbumose may be obtained from different peptone preparations by the following method.

Copper sulphate is added to the peptone solution, when a sticky precipitate of protalbumose separates; the supernatant liquid is cloudy but becomes clear on standing. The clear solution is freed from copper by precipitation with barium ferrocyanide, evaporated, and poured into absolute alcohol; after being collected on a filter, the residue is washed with alcohol and ether, and dried.

A. W. C.

Animal Gum. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1897, 23, 347—362).—Animal gum is the name given by Landwehr to the carbohydrate material of the formula $C_{12}H_{20}O_{10}$, which he obtained from mucin and mucinoid substances. In the case of cartilage, however, Schmiedeberg has shown that the so-called animal gum contains both nitrogen and sulphur, and is, in fact, a mixture of chondroitin and chondroitin-sulphuric acid. Other observers have also noted the presence of nitrogen in this supposed carbohydrate.

In the present research, Landwehr's mode of procedure was followed as closely as possible; the submaxillary gland was used. Various details of difference in the results obtained are noted, and the end-product obtained contained 10—12 per cent. of nitrogen. The process was then repeated, using pure mucin prepared from the submaxillary gland; the end-product here also contained over 11 per cent. of nitrogen. The procedure of heating at 110—150°, which is adopted, converts mucin into a mucin-albumose, and this is precipitable by ferric chloride like the so-called animal gum. It is, however, possible, by the use of acids, to obtain from mucin a reducing substance free from nitrogen, and yielding a crystalline osazone; further details of this part of the work are promised.

W. D. H.

Behaviour of Proteids with Aldehydes. By ERNST O. BECKMANN (*Chem. Centr.*, 1896, ii, 930—932; from *Forsch.-Ber. üb. Lebensm., &c.*, 3, 324. See Abstr., 1895, ii, 375).—With H. SCHARFENBERGER GEN. SERTZ.—To convert 1 gram of gelatin into the insoluble modification, the aqueous solution is mixed with 5—6 drops of 40 per cent. formalin and evaporated on the water bath; 1—2 drops more of formalin are added and the residue is heated for 1—1½ hours at 100°, then digested twice or thrice with water at 60—70°, and dried at 100° until constant. Free acids should previously be neutralised by shaking with precipitated calcium carbonate. A solution of gelatin, which has been deprived of its power of gelatinising by heating for 30—35 hours, nevertheless yields its gelatinose in the insoluble form when treated with formalin. Similarly, albumin, hemialbumose, casein, and protein are rendered insoluble, diastase only to a small extent, whilst gelatin-peptone, albumin-

peptone, and tryptone remain soluble. The method, therefore, serves to show how far the peptonising process has progressed in commercial meat peptones, also to detect gelatin or albumin in meat extracts and sausage meat. Milk to which gelatin-fat emulsion has been added yields little more insoluble residue than pure milk (under $\frac{1}{2}$ per cent.). Formalin-gelatin is, however, completely dissolved by 12 hours' contact with sulphuric acid (1.34 sp. gr.); formalin-casein remains undissolved. Milk should be coagulated by adding a few drops of lactic acid, precipitated by alcohol, the lactose removed by alcohol, the alcohol expelled, the residue extracted with water, the solution neutralised with calcium carbonate and treated with formalin.

With O. ELSNER.—Acetaldehyde behaves like formalin; acetaldehyde does not, except in the absence of water. Acetaldehyde vapour, or its solution in alcohol, benzene, or acetone, slowly hardens dry gelatin films; the acetals have a similar action. Schleich's formalin-gelatin and Blum's protogen (formalin-albumin) have already been introduced into pharmacy.

M. J. S.

Products of the Trypsin-fermentation of Casein. By FRANZ RÖHMANN (*Ber.*, 1897, 30, 1978—1981).—Calf's pancreas (1500 grams) was extracted with chloroform water at 35°, the extract made up to 5 litres; 25 grams of sodium carbonate and 50 c.c. of a 10 per cent. alcoholic solution of thymol were next added, and finally, 500 grams of "nutrose" (sodiocasein), the whole being then allowed to remain at 35° for 8 days; most of the tyrosine separated in the interval. The liquid was then exactly neutralised with hydrochloric acid, filtered, and concentrated, when the rest of the tyrosine separated first, and then the leucine. The latter was purified by freezing the aqueous solution of its hydrochloride, filtering it at a low temperature, and boiling the crystals with 3—4 per cent. ethyl-alcoholic hydrogen chloride, by which means the *hydrochloride* of the *ethylic salt*, $\text{HCl} \cdot \text{NH}_2 \cdot \text{C}_5\text{H}_{10} \cdot \text{COOEt}$, was obtained. This melts at 134°, and in 5 per cent. alcoholic solution has the rotation $[\alpha]_{\text{D}} = +18.4^\circ$. If it is heated in aqueous solution at 200° for several days, the rotation attains a minimum, and a leucine hydrochloride is obtained which yields an ethylic salt melting at 112°, and was found to be identical with leucine prepared from a sample of commercial valeraldehyde (isovaleraldehyde?) that boiled at 92—95°, and had a rotation $\alpha = +38'$ in a 2 dm. tube. By treatment with sodium nitrite and sulphuric acid, the crude leucine was converted into a leucic acid, $\text{OH} \cdot \text{C}_5\text{H}_{10} \cdot \text{COOH}$, which melted at 78°, and had a rotation $[\alpha]_{\text{D}} = -7.6^\circ$; inactive leucic acid, prepared from the inactive leucine, melted at 74°.

C. F. B.

Organic Chemistry.

Californian Petroleum. By CHARLES F. MABERY (*Amer. Chem. J.*, 1897, 19, 796—804).—This paper contains a preliminary account of experiments on the composition of Californian petroleum. The samples examined differ markedly; one from Ventura County, which is very thick and nearly black, is a highly sulphurised oil (0·84 per cent.), and contains a large amount of nitrogen (0·53 per cent.). It unites with more bromine (17·72 per cent.) than Pennsylvanian or Ohio oils, but approximately the same as Canadian oil; probably a considerable portion of the bromine disappears by substitution, since the crude oil contains a large amount of aromatic hydrocarbons. In the lower fractions, the hydrocarbons belong to the series C_nH_{2n} .

Fresno County petroleum is lighter in colour than the foregoing, and has more of a greenish hue. It contains 0·21 per cent. of sulphur, and gave a bromine absorption of 9·07 per cent. A. W. C.

Constitution of Inorganic Compounds, X. Ammoniacal Chromiumthiocyanogen Compounds, By ALFRED WERNER and GEORG RICHTER (*Zeit. anorg. Chem.*, 1897, 15, 243—277).—The authors have examined the two salts known as Reinecke's and Morland's salts which are formed by the action of potassium dichromate on fused ammonium thiocyanate, a mixture of the two salts being obtained by gradually adding the powdered dichromate (40 grams) to fused ammonium thiocyanate (200 grams); the powdered melt is treated with a small quantity of cold water, and the residue, which contains the two salts together with sulphur, is extracted with successive quantities of water at 50° with the addition of a few drops of acetic acid as long as considerable quantities of Reinecke's salt are removed, Morland's salt remaining undissolved.

Reinecke's salt, or, according to Werner's nomenclature, *potassium tetrathiocyanodiamminechromium*, $KCr(NH_3)_2(SCN)_4 \cdot H_2O$, is prepared from the above aqueous extract, in which it is mixed with the ammonium salt, by precipitating it as cadmium salt and decomposing the latter by an aqueous solution of potassium hydrogen sulphide. It crystallises in ruby-red, lustrous plates, or, without water of crystallisation, in scarlet nodules or rhombododecahedra. A determination of the number of ions in the aqueous solutions shows that the salt is easily split into the two ions $Cr(NH_3)_2(SCN)_4$ and K.

From the residue, obtained as mentioned above, Morland's salt is extracted by hot water containing a few drops of acetic acid; it cannot, however, be completely separated from the preceding salt, either by crystallisation from water or from alcohol. When it is converted into the cadmium salt, and the latter is decomposed by a solution of potassium hydrogen sulphate, it yields Reinecke's salt, and the filtrate from the cadmium salt contains guanidine. It is therefore *guanidine tetrathiocyanodiamminechromium*.

Nitrosyl tetrathiocyanodiamminechromium, $Cr(NH_3)_2(SCN)_4NO$, may
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be prepared by adding to a saturated solution of Reinecke's salt, 10 per cent. of its volume of dilute nitric acid (1 acid to 1 water). It is also obtained by treating an acidified solution of Reinecke's salt with nitric peroxide, or, better, with a mixture of nitric oxide and nitrous oxide, or with a nitrite; in the last two cases, a quantitative precipitation is obtained. The crystalline precipitate is washed with water containing a few drops of nitric acid and dried on a porous plate. It crystallises in right-angled, four-sided prisms which are dark reddish-brown by transmitted light; the small crystals are dark brown in reflected light, the larger ones black. It is decomposed by water with partial oxidation into Reinecke's acid. With alkalis, it yields Reinecke's salt and a nitrite; with ammonia, Reinecke's ammonium salt with violent evolution of nitrogen. By careful oxidation with nitric acid, it yields the compound $\text{Cr}(\text{NH}_3)_2(\text{SCN})_3(\text{H}_2\text{O})_2$.

α -Trithiocyanodiaquodiamminechromium, $\text{Cr}(\text{NH}_3)_2(\text{SCN})_3(\text{H}_2\text{O})_2$, has already been obtained by Nordenskjöld (*Zeit. anorg. Chem.*, 1, 137) by oxidising Reinecke's salt with hydrogen peroxide. It is also obtained by the electrolysis of a solution of Reinecke's salt, by oxidising it with potassium chlorate and hydrochloric acid, and by cautious oxidation with warm dilute nitric acid. It is most easily obtained by acting on Reinecke's salt (10 grams) with a concentrated solution of hydrogen peroxide prepared by treating sodium peroxide (10 grams) with a slight excess of concentrated hydrochloric acid and twice its volume of ice; as soon as the violent evolution of hydrogen cyanide commences, the mixture is cooled sufficiently to maintain the temperature below $70-80^\circ$. The mixture is then filtered and the filtrate evaporated at the ordinary temperature until salt commences to separate, when the whole of the trithiocyanodiaquodiamminechromium will have crystallised out; finally, the product is purified by crystallisation from alcohol. When dissolved in water, no ionisation takes place. When treated with ammonia, a mixture of compounds containing more ammonia is obtained, but these have not yet been separated.

β -trithiocyanodiaquodiamminechromium, isomeric with the preceding compound, is obtained along with the preceding salt by the oxidation of Reinecke's salt or the compound $\text{Cr}(\text{NH}_3)_2(\text{SCN})_4\text{NO}$ with nitric acid at 100° . It can be separated from its isomeride by crystallisation from warm water, in which it is less soluble. The α -trithiocyanide crystallises in six-sided tablets with an angle of 120° belonging to the hexagonal system; the β -trithiocyanide in four-sided tablets with angles of 104° and 76° , belonging to the monosymmetric system. The α -compound has a more intense and bluish-red colour; the β -compound is yellowish-red; both compounds when warmed with a concentrated solution of alkali thiocyanate at 100° are at once converted into Reinecke's salt. The two compounds give precipitates with many salts of the heavy metals and with organic bases containing nitrogen, a list being given of those which can be used to distinguish between the isomerides. For example, with cadmium chloride, a 5 per cent. aqueous solution of the α -compound yields a bright red precipitate, the β -compound no precipitate; with guanidine nitrate, the α -compound yields a very characteristic precipitate of elliptical leaflets, the β -compound no precipitate.

E. C. R.

Action of Nitric Acid on Potassium Cobalticyanide. By ÉMILE C. A. FLEURENT (*Compt. rend.*, 1897, 125, 537—538).—When 100 parts of potassium cobalticyanide is heated at 100° for about 10 hours with 500 parts of nitric acid diluted with an equal volume of water, a deep orange-red, fluorescent liquid is obtained, and if after separation of the potassium nitrate by crystallisation this is neutralised with potassium carbonate and mixed with excess of alcohol of 66°, the syrupy mass described by Jackson and Comey (*Abstr.*, 1896, i, 402) separates, but the liquid also contains a product which gives all the reactions of nitroprussides and is most readily separated in the form of the cupric salt. C. H. B.

Hydrates of Magnesium Platinocyanide and their Solubility. By HELLMUTH (BARON) BUXHOEVDEN and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1897, 15, 319—327).—Magnesium platinocyanide is obtained by decomposing the copper salt, suspended in water, with hydrogen sulphide, neutralising the solution of hydrogen platinocyanide thus formed with magnesia, evaporating, and allowing it to crystallise. The red crystals thus obtained always contain less water than is required by the formula $\text{MgPt}(\text{CN})_4 + 7\text{H}_2\text{O}$. The vapour tension of a saturated solution at 19° of the composition $\text{MgPt}(\text{CN})_4 + 37.2\text{H}_2\text{O}$ is 14.4 mm.; when the vapour tension is greater, the crystals deliquesce, and at a lower vapour tension they give off water, whilst at a pressure of 7 mm. the yellow hydrate with $5\text{H}_2\text{O}$ is formed. Homogeneous red crystals with 6.8—6.25 H_2O are obtained at 19° under a vapour tension of 14.4—7 mm. Neither the hydrate with $7\text{H}_2\text{O}$ nor the hydrate with $6\text{H}_2\text{O}$ crystallises from the saturated solution, but from 0—45° crystals with 6.9—6.6 H_2O are obtained; the vapour tension of these crystals is the same as that of the solutions from which they are obtained. When these red crystals are dried, the following hydrates are obtained: at 45°, a bright yellow hydrate with $5\text{H}_2\text{O}$; at 60°, a bright green hydrate with $4\text{H}_2\text{O}$; at 100°, a white hydrate with $2\text{H}_2\text{O}$, and at 210°, the orange-red, anhydrous salt. These hydrates are present in the saturated solutions as follows, from -4.12—45° the red hydrate, above 45° the hydrate with $5\text{H}_2\text{O}$ is formed, from 45—88° the green hydrate is stable, and above 88° the white hydrate is formed.

Tables and curves of the solubility of the various hydrates are given. The results show that each hydrate has a characteristic solubility. E. C. R.

Synthesis of Hexamethylene-glycol Diethyl Ether and other Ethers from Trimethylene Glycol. By ARTHUR A. NOYES (*Amer. Chem. J.*, 1897, 19, 766—781).—*Trimethyleneglycol monethylic ether*, produced by the action of ethylic iodide on the monosodium derivative of trimethylene glycol, is a colourless, pleasant-smelling liquid, miscible with water in all proportions; it boils at 160—161° (corr.), has a sp. gr. = 0.915 at 25°/25°, and an index of refraction 1.416 at 25°.

[With H. M. CHASE.]—The corresponding *diethylic ether*, which is a liquid insoluble in water, possesses a fruity odour, boils at 140—141° (corr.), and has sp. gr. = 0.835 at 25°/25°.

Ethylic γ-chloropropylic ether, prepared by the action of phosphorus
f 2

trichloride on the above monethylic ether, is a liquid boiling at $130\text{--}131^\circ$ (corr.) and of sp. gr. = 0.957 at $25^\circ/25^\circ$. The corresponding bromo-compound is an aromatic-smelling liquid, insoluble in water, boiling at $150\text{--}151^\circ$, and having a sp. gr. = 1.3 at $25^\circ/25^\circ$.

[With GRACE A. VAN EVEREN.] the iodo-compound boils at $130\text{--}134^\circ$ (150 mm.), and has a sp. gr. = 1.585 at $25^\circ/25^\circ$.

Hexamethylene glycol diethylic ether is obtained by the action of sodium on ethylic γ -chloro- (bromo- or iodo-) propylic ether, the best yield (28—30 per cent.) being obtained with either the bromo- or iodo-compounds. It is a colourless liquid, insoluble in water, boiling at 208° (corr.) at ordinary atmospheric pressure, and having a sp. gr. = 0.846 at $25^\circ/25^\circ$; it dissolves in cold concentrated sulphuric acid, and is reprecipitated on adding water. Phosphorus trichloride has little or no action on it.

[With L. H. GOODHUE.]— γ -Ethoxybutyric acid,
 $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$,

was prepared by the action of potassium cyanide on ethylic γ -bromopropylic ether, and subsequent hydrolysis of the nitrile thus obtained; it is a colourless liquid, soluble in water, and boils between $230\text{--}240^\circ$. On submitting the potassium salt of this acid to electrolysis, small amounts of hexamethylene-glycol diethylic ether were obtained.

[With H. H. TOZIER.]—Ethylic γ -phenylpropylic ether, prepared by the action of sodium on a mixture of bromobenzene and ethylic bromopropylic ether, is a liquid of terpene-like odour, boiling at 224° (corr.), and having a sp. gr. = 0.924 at $15^\circ/15^\circ$.

[With C. H. STONE.]—Ethylic γ -ethoxypropylmalonate, obtained by the action of ethylic bromopropylic ether on ethylic sodiomalonate, is a nearly odourless liquid boiling at 273° (corr.) and of sp. gr. = 1.016 at $15^\circ/15^\circ$. On hydrolysis and subsequent elimination of carbonic anhydride from the dicarboxylic acid, δ -ethoxyvaleric acid is obtained as a colourless liquid, soluble in water, boiling at 252° , and having a sp. gr. = 0.994 at $25^\circ/25^\circ$. Another substance was produced in this reaction, but its exact nature was not determined. A. W. C.

Formaldehyde Derivatives of the Polyatomic Alcohols and Acids of the Sugar Group. By K. WEBER and BERNHARD TOLLENS (*Ber.*, 1897, 30, 2510—2514. Compare Abstr., 1894, i, 438; 1896, i, 645).—With formaldehyde and hydrochloric acid, dulcitol yields dimethylenedulcitol, $\text{C}_6\text{H}_{10}(\text{CH}_2)_2\text{O}_6$, which is optically inactive and crystallises in needles melting at $244\text{--}245^\circ$; the dibenzoate $\text{C}_6\text{H}_8\text{O}_4(\text{CH}_2)_2(\text{OBz})_2$, melts at $228\text{--}231^\circ$, and the diacetate at $258\text{--}260^\circ$. Dimethylenerrhamnitol, $\text{C}_6\text{H}_{10}(\text{CH}_2)_2\text{O}_5$, is prepared from rhamnitol and crystallises in needles melting at $138\text{--}139^\circ$. It is dextrorotatory, $[\alpha]_D = +9^\circ$; the monobenzoate forms needles, which melt at $136\text{--}137^\circ$. Monomethylenerrhammonic lactone, $\text{C}_6\text{H}_8\text{O}_5\cdot\text{CH}_2$, is obtained from rhammonic lactone and crystallises in tablets which melt at $178\text{--}180^\circ$; it is laevorotatory ($[\alpha]_D = -85.4^\circ$) and is monobasic towards warm aqueous soda.

Rhamnohexonic acid does not yield any formaldehyde derivative; glucoheptonic lactone, on the other hand, is readily converted into dimethyleneglucoheptonic lactone, $\text{C}_7\text{H}_8(\text{CH}_2)_2\text{O}_7$, which has been ob-

tained in two different forms; the less soluble of these is levorotatory ($[\alpha]_D = -69.5^\circ$) and melts at about 280° , whereas the more soluble has a greater rotation ($[\alpha]_D = -101^\circ$) and melts at about 230° . The acid is readily decomposed by bases, and hence it is extremely difficult to prepare its salts. When saccharin is treated with formaldehyde and hydrochloric acid, a substance is formed which has the composition of *trimethylenedisaccharin*, $C_{12}H_{14}(CH_2)_3O_{10}$, crystallises in needles or plates, melts at $139-140^\circ$, and is levorotatory; $[\alpha]_D = -22.8^\circ$. The presence of the carboxyl group appears to hinder the action of formaldehyde with the adjacent hydroxyl group, the action being further influenced by the configuration of the reacting substance. It appears that substances which yield mucic acid react much less completely than their isomerides; thus mucic acid itself gives no formaldehyde, and the same is true of rhamnohexonic acid, which yields mucic acid on oxidation. Moreover, dulcitol only yields a dimethylene-derivative, whilst its isomerides, mannitol and sorbitol, form trimethylene compounds. A. H.

Preparation of Soluble Starch and Starch Solution. By OTTO FOERSTER (*Chem. Zeit.*, 1897, 21, 41).—To prepare soluble starch, a paste of 20 to 25 grams of starch with water is poured in a thin stream into 200 to 300 c.c. of hot water containing 5 c.c. of concentrated hydrochloric acid, the liquid being stirred until it becomes homogeneous and fairly fluid; heat is then applied and the stirring continued until the liquid is clear and as limpid as water. After cooling, it is filtered, alcohol added to the filtrate, the precipitate which is formed washed with alcohol until free from chlorine, then with ether, allowed to dry in the air, and finally dried by gently warming, or, better, by allowing it to remain over sulphuric acid. To prepare a solution of starch, 20 grams are dissolved as described above, the hydrochloric acid being carefully measured so that it may afterwards be exactly neutralised. The volume of the neutral filtered solution is made up to a litre by adding glycerol. The excess of water can be evaporated after the addition of the glycerol, whereby the stability of the solution is perhaps increased. Both these preparations give blue colorations with iodine. E. W. W.

Soluble Starch. By WIKTOR SYNIEWSKI (*Ber.*, 1897, 30, 2415—2418).—Soluble starch may be obtained by the action of a 9 per cent. solution of sodium peroxide on potato starch suspended in water, and is purified by repeated precipitation by alcohol, when it forms a snow-white, amorphous substance which is almost free from ash; this has the composition $3C_6H_{10}O_5 + H_2O$, is soluble to the extent of 12.5 per cent. in cold water, and in all proportions in hot water; the aqueous solution is not altered by warming on the water bath, and is coloured a pure blue by iodine. The compound is dextrorotatory, but the specific rotation increases with the concentration of the solution. The yield is about 90 per cent. of the original material, the loss being purely mechanical. (Compare Wróblewski, this vol., i, 8.) A. H.

Bromethylamine and Vinylamine. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, 30, 2494—2497).—Sodium hydrogen

carbonate may be used instead of silver carbonate to convert bromethylamine hydrobromide into hydroxyethylcarbamic anhydride (Abstr., 1888, 439), the two substances being warmed together at 40—60°. The anhydride, when boiled with aniline, yields ethylene-

phenylcarbamide, $\begin{matrix} \text{CH}_2 \cdot \text{NPh} \\ \text{CH}_2 \cdot \text{NH} \end{matrix} > \text{CO}$. Bromethylamine hydrobromide

can be converted, with satisfactory yield, into μ -methyloxazoline (Abstr., 1889, 1134) by boiling it with acetic anhydride for 3 hours, distilling off the excess of the anhydride at 60° under diminished pressure, diluting the residue with water, adding excess of potassium hydroxide, cooling meanwhile, and then distilling with steam; μ -methyloxazoline boils at 109.5—110.5°, and its picrate is now found to melt at 159—160°; the lemon-yellow *aurochloride* melts at 184—185°.

Vinylamine reacts with hydrogen sulphide, yielding thioethylamine (Abstr., 1891, 816). C. F. B.

Rapid Polymerisation of Chloral. By JOHN W. MALLETT (*Amer. Chem. J.*, 1897, 19, 809—810).—A specimen of anhydrous chloral, contained in a glass vial with small, drawn-out neck hermetically sealed, polymerised so rapidly as to cause the bursting of the vial. The occurrence is remarkable, inasmuch as the amount of heat evolved in the polymeric change must have been sufficient to produce the effect observed; also the polymeric change must have occurred with a suddenness which is surprising in view of the very gradual transition of liquid chloral into meta-chloral; and it is not easy to imagine what caused the sudden polymerisation, there having been less change of temperature or external disturbance of any kind, at the time when the change occurred, than the specimen had been previously exposed to.

A. W. C.

Glyoxalosazone from Formaldehyde. By HANS VON PECHMANN (*Ber.*, 1897, 30, 2459—2461).—Five compounds have already been isolated from the product of the action of phenylhydrazine on formaldehyde, and in the present paper a sixth is described, which is formed when the reaction takes place in acetic acid solution and the concentration and temperature are so arranged that the liquid remains clear at first. The substance thus formed is identical with glyoxalosazone, and is probably formed by the aldehyde undergoing an aldol condensation, either through the hydrazine or the acetic acid, with formation of glycolaldehyde.

Glyoxalosotetrazone which has been previously described as an oil, crystallises from acetone or alcohol in characteristic, dark-red plates melting at 152°.

J. F. T.

Change of Butyric into Isobutyric Acid. By RUDOLF HUTZLER and VICTOR MEYER (*Ber.*, 1897, 30, 2519—2529).—Erlenmeyer (*Annalen*, 1876, 181, 126) found that a tube containing a cold saturated solution of calcium butyrate which had been used to show the separation of the salt at 100°, remained clear at this temperature after about 10 years' use. By fractional crystallisation of the contents of the tube, he isolated a salt which he regarded as calcium isobutyrate, and which comprised about $\frac{1}{12} - \frac{1}{16}$ of the whole amount of salt present.

The authors have found that this proportion of isobutyrate cannot be detected in this way in a mixture of the two isomeric salts. A trustworthy method for detecting this amount of isobutyrate is to submit the mixture to oxidation with potassium permanganate. The normal acid is chiefly converted into carbonic anhydride, whereas the iso-acid yields acetic acid. Experiments were then made with tubes of resistant glass containing sterile solutions of pure calcium butyrate, and it was found that, after being heated for 6 months at 100° , they no longer gave a precipitate on heating. Isobutyric acid could not be detected in their contents, and the cause of the change was found to be the conversion of a small proportion of the calcium butyrate into the potassium salt by potassium silicate from the glass, calcium silicate being precipitated. The amount of calcium salt is thus diminished to such an extent that the liquid is not saturated at 100° , and hence no precipitation occurs.

A. H.

Conversion of Pentachloroacetone into Trichloroacrylic Acid and Chloromalononic Acid. By PAUL FRITSCH (*Annalen*, 1897, 297, 312—322. Compare Abstr., 1894, i, 490).—*Heptachloropropane*, $\text{CHCl}_2 \cdot \text{CCl}_2 \cdot \text{CCl}_3$, is obtained by heating pentachloroacetone with phosphorus pentachloride in a sealed tube at 180° during 6—8 hours; it has the odour of camphor, melts at 30° , boils at 150 — 151° under a pressure of 50 mm., and at 247 — 248° under atmospheric pressure, slight evolution of hydrogen chloride occurring at that temperature.

Hexachloropropylene, $\text{CCl}_2 \cdot \text{CCl} \cdot \text{CCl}_3$, prepared from the foregoing substance by the action of alcoholic potash (1 mol.), is an oil which has an odour of raspberries. It has a sp. gr. = 1.7652 at $20^{\circ}/4^{\circ}$, and the refractive index $n_D = 1.5091$; it boils at 122 — 123° under a pressure of 50 mm., and at 209 — 210° under atmospheric pressure.

Ethylic orthotrichloroacrylate, $\text{CCl}_2 \cdot \text{CCl} \cdot \text{C}(\text{OEt})_3$, is produced when hexachloropropylene is treated with a slight excess of sodium ethoxide; it has a sp. gr. = 1.2183 at $20^{\circ}/4^{\circ}$, and the refractive index $n_D = 1.4649$. It boils at 149° under a pressure of 50 mm., and at 236 — 237° under atmospheric pressure.

Ethylic trichloroacrylate, $\text{CCl}_2 \cdot \text{CCl} \cdot \text{COOEt}$, obtained by agitating ethylic orthotrichloroacrylate with concentrated hydrochloric acid, is a colourless oil having the odour of peppermint, and boils at 112 — 114° under a pressure of 50 mm., and at 192 — 194° under atmospheric pressure; its sp. gr. = 1.3740 at $20^{\circ}/4^{\circ}$, and the refractive index $n_D = 1.4839$. The *anhydride* of trichloroacrylic acid is insoluble in water, and melts at 39 — 40° , whilst the *amide* crystallises from water in colourless needles, and melts at 96 — 97° ; the *carbamide* forms stellar aggregates of needles, and melts at 165° .

Ethylic α -chloro- β -diethoxyacrylate, $\text{C}(\text{OEt})_2 \cdot \text{CCl} \cdot \text{COOEt}$, formed from ethylic trichloroacrylate by the action of sodium ethoxide, boils at 157 — 159° under a pressure of 50 mm., and at 226 — 230° under atmospheric pressure; it has a sp. gr. = 1.0843 at $20^{\circ}/4^{\circ}$, and the refractive index $n_D = 1.4319$. Agitation with concentrated hydrochloric acid converts the ethereal salt into ethylic monochloromalonate.

M. O. F.

Reaction between Ethylic Isonitrosoacetoacetate and Hydroxylamine Hydrochloride. By MILORAD Z. JOVITSCHITSCH (*Ber.*, 1897, 30, 2421—2422. Compare *Abstr.*, 1896, i, 81).—The yield of oximidomethylisoxazolone may be increased by extracting with ether the mother liquor left after the separation of the compound. If after this treatment it be neutralised with sodium carbonate, a precipitate is obtained, which consists of the compound first prepared by Scholl from isonitrosoacetone and hydroxylamine. A. H.

Colour Reactions of Pyruvic Acid. By LOUIS SIMON (*Compt. rend.*, 1897, 125, 534—536).—When a solution of pyruvic acid is mixed with potassium hydroxide and then with sodium nitroprusside, an intense violet-red coloration is produced, which is turned red by a small quantity of acetic acid, but decolorised by an excess. This reaction is not, however, characteristic, but is shown by a large number of aldehydes, ketones, and their derivatives and condensation products.

On the other hand, if ammonia is substituted for the potassium hydroxide in the foregoing reaction, pyruvic acid gives a beautiful, violet-blue coloration, which is characteristic of pyruvic acid and its metallic and ethereal salts, but does not seem to be given by any other compound except acetophenone, and this is readily distinguished from pyruvic acid by Legal's reaction. A small quantity of acetic acid, but not sufficient to make the liquid acid, is essential to the production of the blue colour, and under these conditions the limit of the reaction seems to be reached when the solution contains 1 part of pyruvic acid in 10,000. In the absence of acetic acid, the coloration is green, not blue, and the limit is reached with 1 part of acid in 5,000 of water. The coloration appears gradually, and its appearance is accelerated by gently heating, but the colour is destroyed by boiling, and also by an excess of acetic acid. Potassium hydroxide changes the blue to deep-red, but addition of acetic acid restores the blue.

When amines of the acetic series are added to a solution of pyruvic acid mixed with sodium nitroprusside, a deep-violet coloration rapidly appears and then rapidly disappears; it is changed to blue by acetic acid, but the blue likewise rapidly disappears. All the amines of the acetic series seem to give this reaction. C. H. B.

[**Beryllium Oxalates.**] By ARTHUR ROSENHEIM and PAUL WOGEL (*Zeit. anorg. Chem.*, 1897, 15, 283—318).—See this vol., ii, 71.

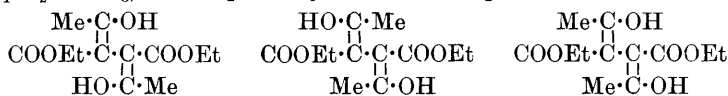
A New Double Platinum Salt. By MAURICE VÈZES (*Compt. rend.*, 1897, 125, 525—527).—When a solution of oxalic acid is added, in rather more than equal molecular proportion, to a hot concentrated solution of potassium platonitrite, the liquid becomes green, and nitrogen oxides are liberated; after a time, however, the liquid becomes golden-yellow, and when cooled yields pale-yellow, prismatic crystals which act on polarised light. These consist of potassium plato-oxalonitrite, and have the composition $K_2PtC_2O_4(NO_2)_2 + H_2O_2$. They are stable in air, lose their water of crystallisation above 100°, and at about 240° decompose completely, with intumescence, into platinum, potassium nitrite, and carbonic anhydride. The salt is very slightly soluble in

cold water, but somewhat soluble in boiling water, and is very stable in solution.

When an excess of oxalic acid is used in the reaction described, the product is the potassium platoxalate, $K_2PtC_2O_4 \cdot 2H_2O$, which crystallises in copper-red needles, and was described by Söderbaum (*Abstr.*, 1886, 532). When the platinum salt is in excess, there is no formation of any intermediate compound analogous to the halogen compounds of the type $K_2PtX(NO_2)_3$ previously described by the author.

The author suggests that when platinum is separated from associated metals in the form of potassium platonitrite, the readiest method of isolating it is to precipitate it as plato-oxalonitrite, and afterwards decompose the latter by heat. C. H. B.

The Isomeric Ethylic Diacetylsuccinates. By LUDWIG KNORR (*Ber.*, 1897, 30, 2387—2389).—The details of the work which is summarised in this preliminary communication will shortly appear in the *Annalen*. The author has succeeded in obtaining no less than five isomerides of ethylic diacetylsuccinate. Three of these are enol-forms (α_1 , α_2 , and α_3), which probably have the configurations



The remaining two are the optically inactive keto-forms (β and γ). Neither of these has yet been resolved into optically active constituents. The following table exhibits the chief properties of these isomerides :

	Melting point.	Index of refraction.	Ferric chloride coloration.	Solubility in light petroleum at 20° (b. p. 50—60°).
β	89°	—	—	1 : 122.5
γ	68°	—	—	1 : 15.3
α_1	liquid	1.5900	brown	1 : 9.7
α_2	21—22°	1.4530	violet	every proportion
α_3	31—32°	1.4392	—	1 : 2.9

The enol-forms have all a faintly acid reaction, and are soluble in aqueous sodium carbonate, but readily become ketonised in this solution. All five isomerides yield the same products when submitted to various chemical reactions.

They are all unstable in the liquid state and in solution, and hence, under these conditions, a state of equilibrium is attained in which the proportions of the various isomerides present can be experimentally determined for different temperatures.

The author considers that the passage of one isomeride into the other is brought about by the migration of the mobile hydrogen atoms. It seems probable, in the light of these results, that liquid tautomeric substances are usually mixtures of the various desmotropic forms of the compound. Solid tautomeric substances, on the other hand, usually represent one definite form. A. H.

Compound of Titanic Acid with Malic Acid. By GEORG BERG (*Zeit. anorg. Chem.*, 1897, 15, 328—330).—The following organic acids do not cause a precipitate in neutral solutions of titanium chloride—malonic, succinic, citric, fumaric, maleic, amidosuccinic, benzoic, ortho-hydroxybenzoic, benzenedisulphonic, phenylacetic, meta- and para-amidobenzoic, hippuric, phthalic, hydroxybutyric, and crotonic, also phenol, trinitrophenol, and resorcinol. White, amorphous precipitates are obtained with acetic, lactic, tribromolactic, tribromacetic, and ψ -cumene-sulphonic acids. A reddish-brown precipitate is produced by nitroso- β -naphthol, a yellow with salicylic acid, and a yellowish-brown with potassium chromate.

Malic acid (also its salts) is the only compound examined which gives a crystalline precipitate; the latter, $2\text{TiO}_2 \cdot \text{C}_4\text{H}_6\text{O}_5 + 6\text{H}_2\text{O}$, crystallises in minute, white prisms, is very stable, and is only slowly decomposed by boiling with water or barium hydroxide solution. It is very sparingly soluble in water, strong acetic acid, or dilute mineral acids, but less so in alcohol. It dissolves slowly in concentrated sulphuric and nitric acids, and at once in concentrated hydrochloric acid. It dissolves at once in caustic alkalis with precipitation of titanic acid, more slowly in ammonia and alkali carbonates. When the crystals are treated with ammonia, they lose $3\text{H}_2\text{O}$ and take up 3NH_3 , and if this compound is allowed to remain exposed to the air it gives off ammonia, and is converted into the compound $2\text{TiO}_2 \cdot \text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NH}_3 + 3\text{H}_2\text{O}$.

Malic acid cannot be employed for the separation of titanic acid from zirconium or iron, as the last two are also precipitated.

E. C. R.

Compounds of Formaldehyde with Uric Acid. By K. WEBER, R. POTT, and BERNHARD TOLLENS (*Ber.*, 1897, 30, 2514—2515).—Diformaldehyde-uric acid, $\text{C}_5\text{H}_4\text{N}_4\text{O}_3 + 2\text{CH}_2\text{O}$, is readily formed, and is monobasic towards one-third normal soda. The mother liquor from its preparation, when treated with alcohol and ether, yields a substance which appears to contain 4—5 mols. of formaldehyde to 1 of uric acid.

A. H.

Aliphatic Derivatives of Hydroxythiocarbamide. By CARL KJELLIN and K. GUSTAV KUYLENSTJERNA (*Annalen*, 1897, 298, 117—129. Compare Tiemann, *Abstr.*, 1889, 1165, and Voltmer, *Abstr.*, 1891, 558).—*Hydroxyethylthiocarbamide*, $\text{NH} \cdot \text{Et} \cdot \text{CS} \cdot \text{NH} \cdot \text{OH}$, is obtained by carefully adding an ethereal solution of hydroxylamine to ethylthiocarbimide dissolved in the same medium; it forms colourless needles or prisms, explodes slightly when touched with a hot glass rod, and melts and decomposes at 109° . The dry substance begins to undergo decomposition after about a week, yielding a mixture of sulphur and ethylcarbamide, but the aqueous and alcoholic solutions are very unstable, precipitation of sulphur occurring in a few minutes; silver and copper sulphides are produced by the action of silver nitrate and Fehling's solutions. Ferric chloride develops an olive-green coloration with the alcoholic solution, whilst the aqueous solution becomes violet; both colours, however, disappear rapidly.

Hydroxymethylthiocarbamide, $\text{NHMe} \cdot \text{CS} \cdot \text{NH} \cdot \text{OH}$, which crystallises in small, colourless, six-sided plates, sinters at 95° , and explodes at

101°; it closely resembles the foregoing compound, and is considerably less stable than that substance.

Hydroxyallylthiocarbamide, $C_3H_5 \cdot NH \cdot CS \cdot NH \cdot OH$, crystallises in microscopic, rectangular plates, forming a colourless, nacreous precipitate when ethereal allylthiocarbimide is added to anhydrous hydroxylamine dissolved in the same medium; it begins to soften at 85°, and fuses completely at 120°. It is extremely unstable, both in the solid state and in solution, yielding sulphur and allylcarbamide; the colour changes with ferric chloride are the same as those exhibited by hydroxyethylthiocarbamide and hydroxymethylthiocarbamide.

Symmetrical hydroxydiethylthiocarbamide, $NH_2Et \cdot CS \cdot NEt \cdot OH$, is prepared by treating an ethereal solution of β -ethylhydroxylamine with ethereal ethylthiocarbimide; it melts at 81°, dissolves sparingly in water and ether, and is readily soluble in alcohol, chloroform, and hot benzene. The crystals from benzene are monosymmetric; $a : b : c = 2.8676 : 1 : 0.8809$. $\beta = 86^\circ 5'$. Hydroxydiethylthiocarbamide may be preserved for any length of time without undergoing change, and the aqueous solution does not yield sulphur when boiled; ferric chloride develops a green coloration with the aqueous or alcoholic solution, passing into bluish-green and reddish-violet on dilution. The *silver* derivative forms slender, silky needles containing $3H_2O$, and resists the action of light; the *gold chloride* derivative is red.

Symmetrical hydroxydimethylthiocarbamide, $NHMe \cdot CS \cdot NMe \cdot OH$, is prepared by adding the calculated amount of sodium methoxide dissolved in methylic alcohol to a solution of β -methylhydroxylamine hydrochloride and methylthiocarbimide in methylic alcohol; it separates from benzene in dimorphous crystals melting at 104°. The colour changes with ferric chloride are similar to those of the foregoing compound. The *silver* derivative forms slender, colourless needles, the *mercurichloride* is dimorphous, and the *aurochloride* is decomposed by water. Ethylic iodide converts hydroxydimethylthiocarbamide into an unstable crystalline compound, which yields ethyl mercaptan when heated with caustic soda.

Hydroxyethylallylthiocarbamide, $C_3H_5 \cdot NH \cdot CS \cdot NEt \cdot OH$, obtained from β -ethylhydroxylamine and allylthiocarbimide, crystallises from benzene in thin, four-sided plates, and melts at 66–67°.

Hydroxymethylallylthiocarbamide, $C_3H_5 \cdot NH \cdot CS \cdot NMe \cdot OH$, is prepared from β -methylhydroxylamine and allylthiocarbimide; it melts at 54°, and crystallises from benzene in beautiful, colourless, monosymmetric prisms. $a : b = 0.60264 : 1$. $\beta = 74^\circ 8'$.

Hydroxymethylethylthiocarbamide, $NHMe \cdot CS \cdot NEt \cdot OH$, obtained from β -ethylhydroxylamine and methylthiocarbimide, crystallises in small, colourless needles, and melts at 122° when heated rapidly.

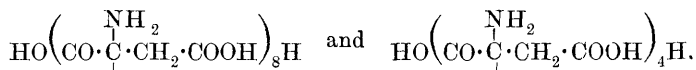
Benzoyloxyallylthiocarbamide, $C_3H_5 \cdot NH \cdot CS \cdot NH \cdot O \cdot CH_2Ph$, is prepared from β -benzylhydroxylamine and allylthiocarbimide; it forms prismatic crystals and melts at 57–58°. M. O. F.

Polyaspartic Acids. By HUGO SCHIFF (*Ber.*, 1897, 30, 2449–2459).—The two anhydrides of aspartic acid prepared by Schaal by the action of carbonic anhydride on asparagine are more easily prepared by heating aspartic acid at 190–200° for 20 hours;

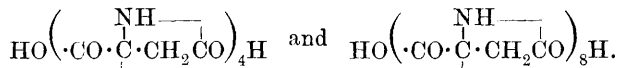
on boiling the product with ten times its weight of water the octo-anhydride (*octoaspartide*), $C_{32}H_{26}N_8O_{17}$, remains undissolved, whilst the tetra-anhydride (*tetraspartide*), $C_{16}H_{14}N_4O_9$, separates from the filtrate on cooling. The filtrate also contains two other substances, namely, *tetraspartic acid*, $C_{16}H_{22}N_4O_{13}$, and a small quantity of *octoaspartic acid*, $C_{32}H_{42}N_8O_{25}$, the latter can also be obtained from its copper salt by treatment with hydrogen sulphide; it forms a vitreous mass which at $190-200^\circ$ passes quantitatively into octoaspartide. Octoaspartide combines with 8 mols. of phenylhydrazine with the formation of a yellow, crystalline *phenylhydrazide*, melting partially and decomposing at $200-205^\circ$. It also combines with aniline with the production of various products, those containing less than 8 mols. of aniline dissolving in alkali with the formation of the corresponding octoaspartanilic acids; on heating with aniline, ammonia is evolved.

Tetraspartic acid crystallises from water in clusters of needles, and is very similar to the octo-acid in its properties.

The author considers the constitution of octoaspartic acid and tetraspartic acid to be respectively



and that of tetraspartide and octoaspartide to be

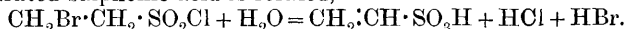


J. F. T.

Aliphatic Sulphonic Acids. By ELMER P. KOHLER (*Amer. Chem. J.*, 1897, 19, 728—752).—From the study of the behaviour of some 23 sulphonic acids towards phosphorus pentachloride, and of the corresponding chlorides towards water, the details of which will appear in subsequent papers, the author is led to the following general conclusions, to which no exceptions have so far been observed.

Monosulphonic acids and $\alpha\alpha$ -chloro- or bromo-monosubstitution products of monosulphonic acids react readily with phosphorus pentachloride in the cold with production of a normal sulphone chloride, which on treatment with water passes back into the acid.

With phosphorus pentachloride, 1 : 2-chloro- or bromo-sulphonic acid reacts in the same way; the chloride, on treatment with water, passes back for the most part into the acid, but at the same time an unsaturated sulphonic acid is formed,



Neither $\alpha\alpha$ - nor $\alpha\beta$ -disulphonic acids react with phosphorus pentachloride in the cold. On heating, in the first case, the product is mainly an $\alpha\alpha$ -chlorosulphonic chloride, together with other chlorine substitution products; and in the second case a disulphonic chloride is formed, which on treatment with water gives principally an unsaturated sulphonic acid, and to a minor extent the regenerated acid.

$\alpha\alpha$ - and $\alpha\beta$ -Sulphocarboxylic acids slowly react with phosphorus pentachloride in the cold. The product is always a chlorine substitution

product of a diacid chloride, which reacts with water in a complicated manner, with different results in different cases.

The special subject treated in this paper is the behaviour of $\alpha\beta$ -ethanedisulphonic chloride towards a number of reagents in order to determine what conditions are most favourable for the production of an unsaturated acid, or the regeneration of the saturated acid.

$\alpha\beta$ -Ethanedisulphonic acid is produced by the oxidation of ethylenic thiocyanate with nitric acid, and crystallises from glacial acetic acid in slender needles melting at 100° . The *sodium* salt is best obtained by boiling ethylenic dibromide and sodium sulphite in concentrated aqueous solution; if the solution is dilute, then sodium monobromethanesulphonate is produced.

$\alpha\beta$ -Ethanedisulphonic chloride, prepared either from the free acid by treatment with phosphorus pentachloride or carbonyl chloride, or from the sodium salt of the acid by warming with phosphorus pentachloride, crystallises from chloroform in large, compact orthorhombic tables melting at 91° . When pure, it can be heated to 150° without a trace of decomposition, but at 160° sulphurous anhydride is slowly evolved and $\alpha\beta$ -chloroethanesulphonic chloride distils over.

All attempts to prepare an unsymmetrical disulphonic chloride failed.

When ethanedisulphonic chloride is acted on by water, an amount of ethylenesulphonic acid corresponding with 90 per cent. of the original substance and 10 per cent. of $\alpha\beta$ -ethanedisulphonic acid are produced.

Methylic, ethylic, propylic and amylic alcohols react with the sulphonic chloride in the same way as water; the amount of unsaturated acid formed diminishes, however, with the increase in the molecular weight of the alcohol. Acids and alkalis also react in the same manner.

Dry ammonia does not act on the sulphonic chloride with production of the corresponding amide, and in alcoholic solution ammonium ethanedisulphonate and anhydrotaurine are formed.

Substituted ammonias behave in a similar manner, aniline, for example, giving rise to anhydrophenyltaurine and *anilidoethanesulphoneanilide*, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{NHPh}$; the latter is an oil which can with difficulty be obtained in colourless plates melting at 75° . The *hydrochloride* crystallises from alcohol in long, colourless needles melting at 171° , and the *monacetyl* derivative melts at 152° .

Acetamide, and acid amides in general, act on the chloride in glacial acetic acid solution, producing mainly ammonium ethanesulphonate.

When the chloride is acted on by sodium acetate (or salts of organic acids in general), sulphurous anhydride is eliminated and 95 per cent. of the original substance is recovered in the form of the sodium salt of ethylenesulphonic acid, and the remainder as sodium ethanedisulphonate.

Zinc dust converts 53 per cent. of the chloride into the zinc salt of $\alpha\beta$ -ethanedisulphonic acid, another substance not fully investigated being also produced.

A. W. C.

Constitution of Meconic Acid. By ALBERTO PERATONER (*Chem. Zeit.*, 1897, 21, 40).—Meconic acid, when boiled with alkalis or

alkaline earths, yields carbonic anhydride, oxalic acid, formic acid, and substances of a gummy nature whose isolation is rendered difficult by the presence of the acids. By the action of barium hydroxide on triethylic meconate, which was prepared by boiling the dry yellow trisilver salt with ethylic iodide and crystallising the product from light petroleum and ethylic alcohol, the author obtained barium oxalate, alcohol, and acetylcarbinylic ethylic ether, but neither carbonic nor formic acid. Since meconic acid belongs to the pyrone group as shown by its conversion into comenic acid (Ost) and since chelidonic acid, which is a pyronedicarboxylic acid, when treated with alkaline earths, splits up into oxalic acid and acetone, the above decomposition indicates the following formula for triethylic meconate

$$\text{COOEt} \cdot \underset{\text{CH} \cdot \text{CO} \cdot \text{COEt}}{\text{C}} - \text{O} - \underset{\text{COEt}}{\text{C}} \cdot \text{COOEt},$$

and hence that the free acid is hydroxy-chelidonic acid. Similar experiments with pyromeconic acid show that this acid probably decomposes into formic acid and acetylcarbinol.
E. W. W.

Nitroketones, Hydroxyketones, Ketochlorides and Ketobromides. By E. C. THEODOR ZINCKE (*J. pr. Chem.*, 1897, [ii], 56, 157—178).—This paper is chiefly theoretical in character, and contains no description of new compounds. By chlorinating tetrachloroparacresol in acetic acid solution, a ketochloride, $\text{CMe} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl}_2 \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{CO}$, is obtained; at a higher temperature and without solvent, the isomeride, $\text{CMeCl} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl} \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{CO}$. A ketobromide, $\text{CMeBr} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl} \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{CO}$, analogous to the last compound, can be obtained in a similar way; it appears to exist only in this configuration, but it sometimes reacts as if it had the constitution $\text{CH}_2\text{Br} \cdot \text{C} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl} \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{C} \cdot \text{OH}$. When oxidised with nitric acid, it yields a compound $\text{OH} \cdot \text{CH}_2 \cdot \text{CBr} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl} \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{CO}$; alkalis convert this into $\text{O} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{C} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl} \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{CO}$, whilst reduction changes it to $\text{CMe} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl} \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{C} \cdot \text{OH}$. Many other reactions of these and similar substances are enumerated, and compared with similar ones observed by Auwers; it is not possible, however, to give a satisfactory abstract of them. It may be said that the ketobromide of tetrabromoparacresol is also considered, as well as the pentabromides from ortho- and meta-cresol, and from metaxyleneol. The formation of a parahydroxyketone by the action of nitric acid on tetrachloroparacresol, &c., has been shown to be preceded by the formation of a paranitroketone, $\text{NO}_2 \cdot \text{CMe} \langle \begin{smallmatrix} \text{CCl} \cdot \text{CCl} \\ \text{CCl} \cdot \text{CCl} \end{smallmatrix} \rangle \text{CO}$.
C. F. B.

Reversible Transformation of Styrene and Metastyrene under the Influence of Heat. By GEORGES LEMOINE (*Compt. rend.*, 1897, 125, 530—533).—The author has investigated the effect of

heat on styrene at 97° , 160° , 240° , 310° and 350° the styrene and metastyrene in the product being separated by distillation under low pressure at a temperature not exceeding 100° . The styrene used boiled at 142 — 144° under a pressure of 751 mm., at about 53 — 54° under a pressure of 1.8 mm. and 48.5 at 0.9 mm. Its sp. gr. was 0.920 at 0° , 0.910 at 12.1° , 0.908 at 16.5° , 0.899 at 27.1° , 0.879 at 51.5° and 0.852 at 87° .

Whether the original substance is styrene or metastyrene, the composition of the product tends towards the same limit under a given set of conditions; provided the temperature is the same throughout the whole of the apparatus, the quantity of styrene that remains unaltered depends on the volume of matter heated, or, in other words, the limit corresponds with a given vapour pressure, as in cases of dissociation. The rate of change is at first somewhat rapid but gradually becomes slower and slower. The limit as determined in flasks of somewhat considerable capacity is not quite the same as the limit determined in narrow glass tubes, the difference being most probably due to the disturbing influence of the walls.

At about 97° , the conversion of styrene into metastyrene is practically complete, but the proportion of styrene remaining increases slightly with the temperature and is 0.9 gram per litre at 310° , the corresponding vapour pressure being 0.4 atmos.

Details of the observations are given in the paper.

C. H. B.

Nitroso-derivatives of Catechol Methyl Ether [Guaiacol]. By A. PROB (*Monatsh.*, 1897, 18, 467—480).—Guaiacol (catechol methyl ether, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} = 1:2$) can be made to yield a nitroso-derivative by dissolving it in alcohol, adding acetic acid, cooling to -2° , adding potassium nitrite gradually, allowing to remain at this temperature, and finally diluting with ice and water. The product, 2-methoxy-1:4-quinone-4-monoxime, $\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NOH}$ or $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NO}$, is identical with Best's paranitrosoguaiacol (*Abstr.*, 1890, 608), and yields the same 2-methoxy-1:4-quinonedioxime when treated with hydroxylamine hydrochloride. When boiled with excess of acetic anhydride, it yields a *monacetyl* derivative, $\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NOAc}$, which melts and decomposes at 156 — 158° ; when reduced with stannous chloride, it yields 4-amido-2-methoxyphenol, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NH}_2$, an unstable base the *hydrochloride* of which was prepared, as also the *triacetyl* derivative, $\text{OAc}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NAc}_2$, which melts at 101° , and yields the hydrochloride of the methoxyamidophenol when it is treated with hydrochloric acid. When the monoxime is heated with water for several hours at 150 — 160° , a small quantity of 2-methoxy-1:4-quinol, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OH}$, is perhaps formed; when it is heated at 100° with potassium methoxide and methylic iodide in the presence of ether, it yields a *methyl ether*, $\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NOMe}$, which melts at 105 — 106° , and forms amidomethoxyphenol when reduced with stannous chloride.

From catechol ethyl ether, yellow 2-ethoxy-1:4-quinone-4-monoxime can be obtained; when heated, it decomposes without melting.

C. F. B.

Derivatives of Guaiacol. By HANS RUPE (*Ber.*, 1897, 30, 2444—2449).—The author has prepared several derivatives of guaiacol containing nitrogen groups in the para-position relatively to the hydroxyl.

Para-nitrosoguaiacol is most conveniently prepared by heating guaiacol, methylic alcohol, sodium methoxide and ethylic nitrite in a closed tube for 12 hours at 100°. *Paranitroguaiacol*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OMe}$ [$\text{NO}_2 : \text{OH} : \text{OMe} = 4 : 1 : 2$], formed from the nitroso-compound on oxidation with alkaline potassium ferricyanide, crystallises from hot water in slender, yellow needles melting at 103—104°. *Dinitroguaiacol*, $\text{OH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{OMe}$ [$\text{OH} : \text{OMe} : (\text{NO}_2)_2 = 1 : 2 : 4 : 6$], melts at 123—124° and is formed when nitric acid acts on nitrosoguaiacol. *Paramidoguaiacol*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{OMe}$, can be prepared either by reducing the azo-compound produced by the combination of diazobenzene chloride with guaiacol by means of tin and hydrochloric acid, or by reducing nitrosoguaiacol with stannous chloride and hydrochloric acid; it crystallises in glistening prisms melting and decomposing at 176—177°; the *hydrochloride* separates from hydrochloric acid in large, pale green crystals. *Paracyanoguaiacol*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{CN}) \cdot \text{OMe}$, prepared from the diazo-compound, is identical with the substance obtained by Markus from vanillin.
J. F. T.

Sitosterol. By RICHARD BURIÁN (*Monatsh.*, 1897, 18, 551—574).—The “germs” of wheat or rye (a refuse product of flour-mills) are extracted with ether, the extracted fat is hydrolysed with alcoholic potash, and the solution is precipitated with calcium chloride. The precipitate of calcium soap and other substances thus obtained is extracted with acetone, the extract is evaporated to dryness and dissolved in ether, the ethereal solution is washed cautiously with dilute hydrochloric acid and potassium hydroxide in succession, and is then evaporated to dryness; the residue is finally crystallised from methylic alcohol. In this way, a substance, $\text{C}_{27}\text{H}_{44}\text{O} + \text{H}_2\text{O}$, is obtained which resembles the cholesterol of bile in external appearance and in composition, but melts at 137·5°, and in ethereal solution has the specific rotation $[\alpha]_D = -26\cdot71^\circ$; it is named *sitosterol* ($\sigma\iota\tau\omicron\varsigma$ = wheat, corn). It is an unsaturated substance, for it forms a *dibromide*, which does not crystallise easily, and is difficult to purify; it melts and decomposes at about 98°. It also forms a *monacetate*; this melts at 127° after softening at 124·5°, and yields a *dibromide* which also crystallises with difficulty; a *propionate* and *benzoate*, melting respectively at 108·5° and 145—145·5°, were also prepared. *Sitosterylic chloride*, $\text{C}_{27}\text{H}_{43}\text{Cl}$, can be obtained by the action of phosphorus pentachloride on sitosterol; it melts at 87·5° after softening at 82° and is reduced by sodium in boiling amyl alcoholic solution to *sitostene*, $\text{C}_{27}\text{H}_{44}$, which melts between 61° and 68°, according to the rapidity with which it is heated, has in ethereal solution the specific rotation $[\alpha]_D = -38\cdot79^\circ$, and is an unsaturated hydrocarbon, forming a *dibromide* which crystallises with difficulty, and melts between 105—110° after softening at 70°.

The methyl alcoholic mother liquor from the sitosterol contains another substance, *parasitosterol*, which melted at 132·5°; after con-

version into the acetate and recovery from the latter by hydrolysis with sodium methoxide, at 127.5° ; it resembles sitosterol in appearance. This substance appears also to have the composition $C_{27}H_{44}O$, but in ethereal solution it has the specific rotation $[\alpha]_D = -20.8^\circ$, and its *monacetate* melts at $115-120^\circ$, and forms a *dibromide* which melts at 112° after softening at 104.5° .

Finally, a tabulated list is given of all the phytosterols (vegetable cholesterols) at present known, with their specific rotations, and the melting points and crystalline form of themselves and their acetates and benzoates.

C. F. B.

Formation of Chains: XVII. Orthotoluidine and Metatoluidine; XVIII. Paratoluidine; XIX. Metaxylidine. By CARL A. BISCHOFF (*Ber.*, 1897, 30 2464—2468, 2469—2475, 2476—2480. Compare this vol., i, 10).—Aromatic amines, $R_1 \cdot NH_2$, were heated with ethylic salts of α -bromo-acids, $CR_n R_{n+1} Br \cdot COOEt$. The products of the reaction are $R_1 \cdot NH \cdot CR_n R_{n+1} \cdot COOEt$ and $R_1 \cdot NH_3 Br$; to determine the extent to which the reaction has taken place, the amine hydrobromide was washed with chloroform and weighed; the error was not greater than ± 2 per cent. As a rule, the temperature employed was 120° , and the heating was continued for 4 hours; experiments were also made at $130-135^\circ$ and at 180° , and the products of these were submitted to fractional distillation, the fractions being weighed and a fractionation curve constructed. Some experiments were also made at 100° . The numbers in Table I. give the extent, in percentages of the theoretical maximum, to which the reaction takes place between the amines and ethylic salts there tabulated; the amount of reaction between the amines and certain acids, $R_n \cdot COOH$, was also determined, each pair of substances being heated together for 1 hour at 100° , the product being, of course, a substance of the type $R_n \cdot CO \cdot NHR_1$; Table II. gives the results.

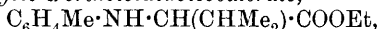
TABLE I.

Ethylic salt.		Aniline.	2-Toluidine.	3-Toluidine.	4-Toluidine.	1:3:4-Xylidine.
At 100° .	Bromopropionate	95	54	94	92	91
	Bromophenylacetate..	68	43	47	43	68
	Bromisobutyrate	29	19	62	38	19
At 120°	Bromopropionate	94	97	94	93	96
	Bromobutyrate	86	84	87	92	89
	Bromisobutyrate	66	40	81	77	61
	Bromisovalerate	23	15	19	38	14

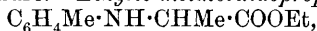
TABLE II.

R_n ($R_n \cdot COOH$).	2-Toluidine.	4-Toluidine.	1:3:4-Xylidine.
H	92.2	95	94.6
CH_3	17.6	81.6	26.2
CH_2Me	7.2	11.9	3.6
$CH_2Et \cdot CH_2$	4.2		1.8
CH_2Et	2.7	3.0	0.9
$CHMe_2$	1.4	3.4	0.3
$CHMe_2 \cdot CH_2$		0.0	
$OH \cdot CH_2$	28.4	44.6	20.4
$OH \cdot CHMe$	20.4	26.5	11.8
$OH \cdot CHPh$	14.1	14.7	6.1
$OH \cdot CHEt$	14.5		4.9
$OH \cdot CMe_2$	0	1.2	2.4

The following new substances were prepared in the course of the investigation. *Ethyllic α-orthotoluidoisovalerate*,



melts at 30° and boils at 282—284° under 763 mm. pressure; the corresponding *acid* melts at 101°, and loses carbonic anhydride when distilled, yielding *isobutylorthotoluidine*, which boils at 230—235° under 758 mm. pressure. *Ethyllic metatoluidopropionate*,



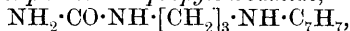
boils at 271—276° under 767 mm. pressure; *ethyllic metatoluidobutyrate*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CHEt}\cdot\text{COOEt}$, at 281—285° under 745 mm.; and *ethyllic metatoluidoisobutyrate* at 270—273° under 753 mm., and at 205—210° under 104 mm. pressure; *ethyllic α-metatoluidophenylacetate*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{COOEt}$, melts at 109°. *Ethyllic α-paratoluidoisovalerate* boils at 295° under 753 mm. pressure; the corresponding *acid* melts at 110°. *Ethyllic α-paratoluidophenylacetate* melts at 85—86°. When paratoluidine is heated with chloracetamide, eventually to 150°, *paratolylimidodiacetamide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:(\text{CH}_2\cdot\text{CO})_2\cdot\text{NH}$, melting at 195°, is produced; whilst in the presence of sodium acetate, paratoluidacetamide is formed instead. Paratoluidine with α-bromopropionamide at 80° yields toluidopropionamide, and at 150—180°, α-*paratoluidopropionic paratoluidide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, which melts at 158°. With α-bromobutyramide and α-bromisobutyramide at 120—130°, it yields respectively α-*paratoluidobutyric* and α-*paratoluidoisobutyric paratoluidides*, melting at 138° and 144°. *Ethyllic α-metaxylidopropionate*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{CHMe}\cdot\text{COOEt}$, melts at 42° and boils at 274—275° under 753 mm. pressure. *Ethyllic α-metaxylidobutyrate*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{CHEt}\cdot\text{COOEt}$, boils at 285—290° under 753 mm. *Ethyllic metaxylidophenylacetate*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{CHPh}\cdot\text{COOEt}$, melts at 90·5°.

C. F. B.

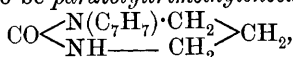
Nitrosoanilines. By M. C. SCHUYTEN (*Chem. Zeit.*, 1897, 21, 24).—By passing nitric oxide gas through an alcoholic solution of aniline, the author obtained nitraniline, but no nitroso-derivative.

E. W. W.

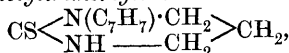
Paratolyltrimethylenediamine and γ-Iodopropylamine. By MARTIN FRÄNKEL (*Ber.*, 1897, 30, 2497—2510).—By heating γ-bromopropylphthalimide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\text{Br}$ (1 mol.), with paratoluidine (2 mols.), eventually at 150°, yellow *paratoluidopropylphthalimide*, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_3\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, melting at 134—136°, is obtained; the white *hydrochloride* melts at 198°, and is decomposed by water. If a relatively smaller amount of the toluidine is used, the product is yellow *paratoluidodipropyldipthalimide*, $(\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_3)_2\cdot\text{N}\cdot\text{C}_7\text{H}_7$, melting at 124°. When paratoluidopropylphthalimide is boiled with 20 per cent. hydrochloric acid, *paratolyltrimethylenediamine*, $\text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, is formed (Balbiano, *Abstr.*, 1889, 1216); this boils at 283° under 763 mm. pressure, and has a sp. gr. = 1·0253 at 15°; the *hydrochloride*, with 2HCl, melts at 257°, the yellow *platinochloride* at 205°, and the greenish-yellow *picrate* at 113°; the base absorbs carbonic anhydride from the air. With potassium cyanate and hydrochloric acid, it forms *paratoluidopropylcarbamide*,



which melts at 152° losing ammonia; after prolonged heating at 212° , the residue is found to be *paratolyltrimethylenecarbamide*,

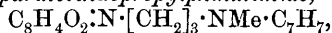


melting at 207° . With potassium thiocyanate and hydrochloric acid at 140° , it yields *paratolyltrimethylenethiocarbamide*,



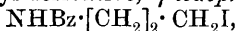
melting at 188° . With carbon bisulphide, it forms the *dithiocarbamate*, $\text{NH}(\text{C}_7\text{H}_7) \cdot [\text{CH}_2]_3 \cdot \text{NH} \cdot \text{CS} \cdot \text{SNH}_3 \cdot [\text{CH}_2]_3 \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, which melts at 125° , and decomposes at that temperature, or when boiled with water, into hydrogen sulphide, paratolyltrimethylenediamine, and paratolyltrimethylenethiocarbamide. With nitrous acid, it yields *amidopropyl-paratolylnitrosamine*, $\text{NH}_2 \cdot [\text{CH}_2]_3 \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{NO}$, the *hydrochloride* of which melts at 175° ; the nitrosamine itself is an oil which decomposes when distilled, and absorbs carbonic anhydride from the air. When paratoluidopropylphthalimide is heated with methylic iodide at 125° , the product is γ -*iodopropylphthalimide*, $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{N} \cdot [\text{CH}_2]_3 \cdot \text{I}$, melting at 88° , and methylparatoluidine.

By heating γ -bromopropylphthalimide with methylparatoluidine at 170° , yellow *methylparatoluidopropylphthalimide*,

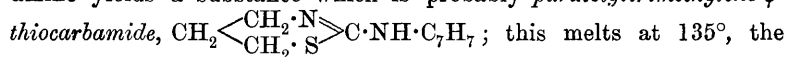


melting at 125° , is obtained.

γ -Iodopropylphthalimide (see above) is more conveniently obtained by boiling γ -bromopropylphthalimide with aqueous alcoholic sodium bromide. When boiled with hydriodic acid of boiling point 127° , it yields γ -*iodopropylamine*, $\text{NH}_2 \cdot [\text{CH}_2]_3 \cdot \text{CH}_2\text{I}$, isomeric with a compound previously prepared by Hofmann and by Gabriel (Abstr., 1897, i, 136). This is an unstable oil; the *hydriodide* melts at 166° , the yellow *picrate* at 134 — 135° ; its benzoyl derivative, γ -*iodopropylbenzamide*,



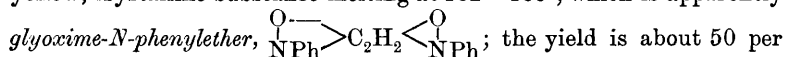
melts at 68° , and reacts with paratoluidine at 170° , forming crystalline *benzoparatolyltrimethylenediamide*, $\text{NHBz} \cdot [\text{CH}_2]_3 \cdot \text{NH} \cdot \text{C}_7\text{H}_7$. With paratolylthiocarbimide, $\text{CS} \cdot \text{NC}_7\text{H}_7$, in ethereal solution, γ -iodopropylamine yields a substance which is probably *paratolyltrimethylene- ψ -thiocarbamide*,



this melts at 135° , the *hydriodide* at 200° , the reddish-yellow *platinochloride* at 208° , and the yellow *picrate* at 170° .

C. F. B.

Action of Diazomethane on Nitrosobenzene. By HANS VON PECHMANN (*Ber.*, 1897, 30, 2461—2463).—The action of diazomethane on nitrosobenzene in ethereal solution leads to the formation of a yellow, crystalline substance melting at 182 — 183° , which is apparently



the yield is about 50 per cent. of the theoretical, and phenylhydroxylamine is formed as a bye-product, which makes it probable that part of the nitrosobenzene has acted as an oxidising agent. This new substance has been prepared by Bamberger from formaldehyde and phenylhydroxylamine (*Vierteljahrsschr.*

d. naturforsch. Ges. in Zürich, 1896, 178); acids decompose it into glyoxaldehyde and phenylhydroxylamine, from which two substances it can be prepared synthetically; heating with acetic anhydride converts it into oxanilide, or derivatives of this. C. F. B.

Diazocyanides and Double Salts of Diazonium Cyanides. By ARTHUR R. HANTZSCH and KARL DANZIGER (*Ber.*, 1897, 30, 2529—2548. Compare Abstr., 1895, i, 348).—The diazonium cyanides cannot be obtained in the pure state, but their double salts are formed when a solution of a diazonium chloride is treated with silver cyanide or a neutralised solution of potassium cyanide. The presence of hydroxyl ions, which are invariably present in ordinary potassium cyanide solution, causes the formation of the insoluble *syn*-diazocyanide. The double salts with silver cyanide are colourless, soluble in water, and of neutral reaction, and are at once decomposed by acetic acid, whilst in aqueous solution they gradually decompose, forming nitrogen, hydrogen cyanide, silver cyanide, and a phenol. They thus closely resemble the double cyanide of silver and potassium. This behaviour also renders it probable that the free diazonium cyanide itself would resemble potassium cyanide, and therefore differ essentially from the normal diazocyanide, which is stable towards acids.

ψ-Cumenediazonium silver cyanide, $C_6H_2Me_3 \cdot \overset{\text{N}}{\underset{\text{N}}{\text{N}}} \cdot \text{CN}, \text{AgCN}$, has only

been obtained in aqueous solution and is prepared from the diazonium iodide and silver cyanide. It readily forms azo-colouring matters. *Parabromodiazonium silver cyanide*, $C_6H_4Br \cdot \overset{\text{N}}{\underset{\text{N}}{\text{N}}} \cdot \text{CN}, \text{AgCN}$, has been

obtained in small quantity in the form of a crystalline powder, which explodes at 119—120°.

Of the stereoisomeric diazocyanides, $R \cdot \text{N} \equiv \text{N} \cdot \text{CN}$, the *syn*- or normal compounds, $\overset{\text{R}}{\text{CN}} \cdot \overset{\text{N}}{\underset{\text{N}}{\text{N}}}$, are the primary products of reaction, are labile,

have a low melting point, readily form azo-colouring matters, and can be directly decomposed into nitrogen and a nitrile. The *anti*- or *iso*-diazocyanides, on the other hand, are stable, have a high melting point, and do not easily form azo-colouring matters or decompose into nitrogen and a nitrile. As will be seen from the description of the various compounds, the presence of negative groups increases the stability of the *syn*-form, a group having a greater effect in the *ortho*- than in the *para*-position; the presence of halogens also diminishes the readiness with which both series undergo reaction. Diorthocyanides are decomposed into nitrogen and a dihalogen derivative of benzene by alcohol and an alkali, whereas all other halogen diazocyanides are thus converted into diazoimido-ethers.

Alcohol radicles appear to be unfavourable to the formation of stable cyanides of either series.

Syn-parabromobenzenediazocyanide, $C_6H_4Br \cdot \overset{\text{N}}{\underset{\text{N}}{\text{N}}} \cdot \text{CN}$, is obtained by add-

ing aqueous potassium cyanide to parabromobenzenediazonium chloride solution at -10°; it forms yellow needles melting at 42°, reacts

violently with precipitated copper, and forms bromobenzeneazophthol with β -naphthol. If kept for a day, or dissolved in alcohol and precipitated by water, at the ordinary temperature, it passes into the *anti*-cyanide, $\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{N} \\ || \\ \text{N} \cdot \text{CN} \end{smallmatrix}$, which crystallises from light petroleum

in brown needles melting at $129-130^\circ$; this is indifferent towards β -naphthol and copper powder. *Syn-paraiodobenzenediazocyanide* is yellowish-brown and melts at 48° ; the *anti*-cyanide crystallises in reddish-brown needles and melts at 152° . *Syn-orthobromobenzenediazocyanide* forms yellow needles and melts at 51° ; it does not pass into the isomeride at the ordinary temperature, but when precipitated by water from alcoholic solution at the ordinary temperature, a small quantity of the *anti*-compound is formed, which melts at $107-108^\circ$. *Syn-metabromobenzenediazocyanide* forms very unstable needles melting at $25-26^\circ$. The *anti*-salt has not yet been obtained.

Syn-2:4-dibromobenzenediazocyanide melts at $70-71^\circ$, is stable, and only passes into the *anti*-salt at the summer temperature; the latter crystallises from dilute alcohol in reddish-brown plates melting at 141° . Both forms are converted by alcohol and hydrogen chloride into 2:4-dibromodiazocarbamide, $\text{C}_6\text{H}_3\text{Br}_2 \cdot \text{N}_2 \cdot \text{CO} \cdot \text{NH}_2$, which crystallises in orange-coloured needles melting at 194° . Alcoholic potash converts it into *potassium dibromodiazocarboxylate*, which forms golden-yellow plates and yields a yellow precipitate of the *free acid* on acidification. The *syn-dichlorocyanide* changes more readily than the dibromo-compound into the *anti*-compound. *Syn-2:4-diiodobenzenediazocyanide* melts at 96° , the *anti*-cyanide at 186° . *Syn-3:4-dibromobenzenediazocyanide* melts at $56-57^\circ$; it changes in a few days into the *anti*-cyanide, which crystallises from light petroleum in small, brown needles melting at $100-101^\circ$. *Syn-2:5-dibromobenzenediazocyanide* melts at $42-43^\circ$, and in a few days changes into the *anti*-cyanide, which crystallises from dilute alcohol in brick-red needles melting at $122-123^\circ$. *Syn-3:5-dibromobenzenediazocyanide* melts at 60° , and decomposes if kept; the *anti*-compound melts at 85° . *Syn-2:6-dibromobenzenediazocyanide* melts at $44-45^\circ$, and decomposes completely when kept, or if it is precipitated from alcoholic solution at the ordinary temperature. The *anti*-compound has not been obtained.

Syn-2:4:6-tribromobenzenediazocyanide, which forms yellow plates melting at $59-60^\circ$, is remarkably stable, does not change when kept, and only reacts slowly with β -naphthol and with copper; with alcohol and soda, it yields tribromobenzene and nitrogen. The *anti*-salt can only be obtained with difficulty and forms brownish-red crystals melting at 147° ; alcohol and caustic soda convert it into the corresponding diazoimidoether. *Syn-symmetrical-2:4:6-trichlorobenzenediazocyanide* is much less stable than the tribromo-compound; the *anti*-compound has not been obtained. *Syn-2:4:5-trichlorobenzenediazocyanide* melts at 55° and is very stable; the *anti*-cyanide crystallises in red needles melting at $100-101^\circ$. Alkyl-diazocyanides can only be prepared by adding the diazonium salt to an excess of potassium cyanide solution at -12° . The *toluene*-derivative is oily, the *asymmetrical metaxylenediazocyanide* is solid, but rapidly decomposes.

Syn-ψ-cumenediazocyanide forms dark red crystals melting at 38—39°; the *anti*-compound has not been prepared. *Syn-bromometaxylenediazocyanide* melts at 49—50° and readily passes into the *anti*-compound which melts at 64—65°. *Syn-paramethoxybenzenediazocyanide* melts at 50°, and changes in a few days into the *anti*-cyanide melting at 122°.

Syn-α-naphthalenediazocyanide melts at 57—58° and changes completely and readily into the *anti*-cyanide, which crystallises in reddish-brown needles and melts at 116°.

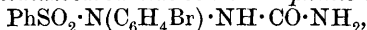
Syn-β-naphthalenediazocyanide melts at 51—52° and rapidly passes into the *anti*-compound, which crystallises from hot alcohol in yellowish red needles melting at 131°. A. H.

Additive Products of Azo- and Diazo-compounds with Benzenesulphinic Acid. By ARTHUR R. HANTZSCH and R. GLOGAUER (*Ber.*, 1897, 30, 2548—2559. Compare *Abstr.*, 1897, i, 222).—Azo-compounds and both normal and iso-diazo-compounds unite with benzenesulphinic acid to form colourless compounds when an alcoholic solution of the azo- or diazo-compound is added to a similar solution of benzenesulphinic acid. These are stable towards acids, but are decomposed by alkalis, are probably derivatives of hydrazobenzene, and are formed by direct addition. When the solutions are mixed in the inverse order, phenylsulphones are formed as a rule. Diazonium compounds, on the other hand, only react with benzenesulphinic acid to form diazosulphones, so that this reaction affords a purely chemical proof of the constitution of the normal diazocyanides, which combine with benzenesulphinic acid, and therefore cannot have the diazonium formula. Both *syn*- and *anti*-diazo-compounds yield the same additive product, the asymmetry of the azo-group disappearing when a derivative of ammonia is produced. On decomposition with alkalis, the additive product formed from either diazocyanide yields benzenesulphinic acid and the *anti*-diazocyanide, so that the *syn*-cyanide can in this way be converted into its isomeride.

Phenylsulphonehydrazobenzene (benzenesulphinic acid azobenzene), $\text{NHPh} \cdot \text{NPh} \cdot \text{SO}_2\text{Ph}$, is obtained by adding an alcoholic solution of azobenzene to a similar solution of benzenesulphinic acid; it crystallises in pure white, silky needles melting at 107°. *Phenylsulphonehydrazochlorobenzene cyanide*, $\text{PhSO}_2 \cdot \text{N}(\text{C}_6\text{H}_4\text{Cl}) \cdot \text{NH} \cdot \text{CN}$, is prepared from parachlorobenzenediazocyanide and decomposes at 131°; the corresponding *bromo*-derivative decomposes at 127°.

Syn-2 : 6-dibromobenzenediazocyanide, which is itself very unstable, yields a remarkably stable *hydrazo*-compound with benzenesulphinic acid which melts at 168°; aqueous potash converts it into a coloured stable substance which also melts at 168°, and is probably the *anti*-cyanide. *Syn*-tribromobenzenediazocyanide readily unites with benzenesulphinic acid, in whatever order the solutions are mixed, to form a colourless compound, which decomposes at 162°; treatment with aqueous potash produces the *anti*-cyanide, which is best prepared in this way.

Parabromobenzenediazocarbamide-benzenesulphinic acid,



is formed by the combination of its constituents and melts at 151°; the

additive compound formed from chlorobenzenediazoimido-ether melts at 138°.

Benzenediazophenylsulphone and bromobenzenediazoimidocyanide also form similar compounds, the derivative of the latter decomposing at 118°. The two stereoisomeric nitrobenzenediazocyanides do not appear to behave in this way; phenylenediazosulphide does not unite with benzenesulphinic acid, whilst ethylic diazoacetate is decomposed by it even at low temperatures. The compound formed from orthodiazobenzoic acid and benzenesulphinic acid, which was previously described by Hantzsch and Singer, probably possesses the hydrazo-constitution, $C_6H_4 \begin{matrix} \text{CO} \text{---} \text{O} \\ \diagup \quad \diagdown \\ N(SO_2Ph) \cdot NH \end{matrix}$ or $C_6H_4 \begin{matrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ NH \cdot N \cdot SO_2Ph \end{matrix}$. *Orthodiazobenzoparatoluenesulphinic acid*, $C_6H_4 \begin{matrix} \text{CO} \text{---} \text{O} \\ \diagup \quad \diagdown \\ N(SO_2C_7H_7) \cdot NH \end{matrix}$, melts and

decomposes at 160°, and is at once decomposed by caustic alkalis into toluenesulphinic acid and salicylic acid.

Orthodiazobenzoparabromobenzenesulphinic acid melts at 181°, and yields a very unstable, yellow salt with concentrated aqueous soda.

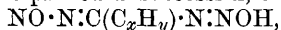
A. H.

Tetrazotic, Oxytetrazotic, and Dioxytetrazotic Acids. By WILHELM C. LOSSEN (*Annalen*, 1897, 297, 322—325. Compare Abstr., 1892, 51).—Ferric chloride is a useful agent for recognising many dioxytetrazotic acids, as, for example, benzenyldioxytetrazotic acid and paratolenyldioxytetrazotic acid, with which it develops a red coloration, and forms an iron derivative which dissolves in ether.

Benzenyldioxytetrazotic acid and many of its salts are decomposed in accordance with the equation $C_6H_5 \cdot CN_4O_2H = C_6H_5 \cdot CN + N_2 + HNO_2$ under the influence of feeble bases. In the case of dioxytetrazotic acid, this decomposition is spontaneous, nitrous acid being set free; moreover, potassium benzenyldioxytetrazotate liberates nitrogen and yields potassium benzoate when the solution is boiled; the occurrence of one or other of these changes depends, not only on the circumstances of the experiment, but also on the nature of the acid.

It is noteworthy that benzenyldioxytetrazotic and paratolenyldioxytetrazotic acids are readily converted into the amidines from whence they are derived; treatment of the former substance with hydrochloric acid followed by ammonia gives rise to the benzenylamidine salt of benzenyldioxytetrazotic acid.

In spite of the fact that all attempts to couple the dioxytetrazotic acids with phenols have proved unsuccessful, the formula



most nearly expresses their chemical behaviour, although it must be admitted that they differ from other diazo-compounds in forming additive compounds, instead of diazoamido-derivatives, with amines.

M. O. F.

Benzenyldioxytetrazotic Acid. By WILHELM C. LOSSEN and MAX GRONEBERG (*Annalen*, 1897, 297, 325—349. Compare Lossen and Mierau, Abstr., 1891, 1038).—The benzenylamidine salt of benzenyldioxytetrazotic acid crystallises from alcohol in regular quadratic leaflets, and from water in yellowish, prismatic crystals; it

explodes at 178° , or at 171° when heated slowly. The potassium salt is also yellowish, and when the aqueous solution is boiled, yields nitrogen and potassium benzoate in quantitative amount. The *ammonium* salt, obtained by adding ammonium chloride to a solution of the potassium salt, crystallises in long, colourless prisms; it dissolves readily in water and alcohol, explodes at 137° , and when heated with water yields nitrogen and ammonium benzoate. The *hydrazine* salt forms microscopic, six-sided plates, scarcely soluble in cold water or alcohol, and insoluble in ether; it explodes at 60° , and also when rubbed in a mortar. When an alcoholic solution of the hydrazine salt is heated on the water-bath, nitrogen is liberated at 35° , two-fifths of the theoretical amount being obtained; benzonitrile is also produced, along with ammonium benzenyldioxytetrazotate, whilst, on one occasion, benzenylamidine benzenyldioxytetrazotate was formed. The *aniline* salt of benzenyldioxytetrazotate is obtained as a yellowish-white powder which is insoluble in ether, and dissolves with difficulty in water; it crystallises from alcohol in white needles, and explodes at 93° . When the salt is treated with boiling water, nitrogen, benzonitrile, and phenol are produced, along with an amorphous compound having the formula $C_{22}H_{17}N_3O$. The *paratoluidine* salt also crystallises from alcohol in colourless needles, decomposes at 105° , and when boiled with water yields benzonitrile, paracresol, and nitrogen.

No definite product is obtained by the action of dimethylaniline on dioxytetrazotic acid. When a solution of the base in normal sulphuric acid is added to an aqueous solution of the potassium salt, and the liquid boiled, an intense green coloration is developed, and gas is evolved, whilst a brown, tarry substance separates; this compound is precipitated from chloroform by light petroleum, and has the composition $C_{24}H_{32}N_4O$.

The *phenylhydrazine* salt of benzenyldioxytetrazotic acid is very sparingly soluble in water, and crystallises from alcohol in needles which explode at 90° ; when heated with water, it yields benzonitrile, and the same change occurs spontaneously.

The behaviour of benzenyldioxytetrazotic acid towards ferric chloride is very characteristic. On treating the potassium salt with neutral ferric chloride, a dark, violet-brown precipitate is at once formed, and yields a dark, reddish-brown solution on agitation with ether; the ethereal solution, however, is very unstable, and if separated from the aqueous liquid, gradually deposits a reddish-brown powder, and becomes colourless, yielding benzoic acid on evaporation. If the original precipitate is filtered before agitation with ether, it explodes feebly when heated in the dry state; treatment with caustic potash gives rise to potassium dioxytetrazotate.

Experimental details relating to the decomposition of benzenyldioxytetrazotic acid by acids, and the regeneration of benzenylamidine (compare foregoing abstract) are described in the paper. M. O. F.

Paratolenyldioxytetrazotic Acid. By WILHELM C. LOSSEN, FRANZ HESS, CARL KIRSCHNICK, and PAUL SCHNEIDER (*Annalen*, 1897, 297, 349—353. Compare foregoing abstracts).—The *paratolenyl-*

amidine salt of paratolenyldioxytetrazotic acid, $C_8H_8N_4O_2, C_8H_{10}N_2$, is obtained by adding a concentrated solution of potassium nitrite (38 grams) to a concentrated solution of paratolenylamidine hydrochloride (20 grams), dissolving the crystalline precipitate in cold water, and treating the solution with 63 per cent. nitric acid (11 grams). It crystallises from boiling water in yellowish, rhombic leaflets, and yields rectangular prisms when recrystallised from alcohol; in the latter form, it explodes at $195-198^\circ$. The *potassium* salt separates from concentrated, aqueous solutions in colourless leaflets containing $1H_2O$, which is removed in the desiccator; even in the moist condition, the salt is highly explosive, and the aqueous solution yields nitrogen and paratoluic acid when boiled or submitted to the influence of sunlight. The *ammonium* salt crystallises in colourless needles, and explodes at 130° ; the alcoholic and aqueous solutions, when boiled, liberate nitrogen, and yield ammonium toluate on evaporation. The *pyridine* salt is crystalline, and explodes when heated; it dissolves in water and alcohol, but is insoluble in ether. The *hydroxylamine*, *aniline*, *barium*, and *silver* salts are explosive solids. Ferric chloride has the same action on the potassium salt as on the potassium salt of benzenyldioxytetrazotic acid, yielding a highly unstable precipitate which forms a brownish-red solution in ether. M. O. F.

Decomposition of Potassium Paratolenyldioxytetrazotate by Hydrochloric Acid. By WILHELM C. LOSSEN and FRANZ HESS (*Annalen*, 1897, 297, 354—370. Compare foregoing abstracts).—The action of mineral acids on salts of paratolenyldioxytetrazotic acid proceeds in the same direction as in the case of benzenyldioxytetrazotic acid, the chief product being paratoluenitrile. If, however, a cold, saturated solution of potassium paratolenyldioxytetrazotate is treated with 1 mol. proportion of a normal solution of hydrochloric acid, and agitated during five minutes, a dark green substance is precipitated, which, if allowed to remain in the liquid, gradually becomes converted into toluonitrile, yielding nitrogen. The greenish-yellow compound (*Säurefällung*) must be collected, washed with alcohol and ether, rapidly dried in a current of air, and preserved in thin, interrupted layers, protected from the light; even then the substance becomes colourless spontaneously, but if these precautions are not observed, a violent explosion takes place. It is evident that this substance does not consist of free paratolenyldioxytetrazotic acid, as the precipitation is slow, although the product is insoluble in water; moreover, it is found that the filtrate contains in the unaltered state upwards of one-half the dioxytetrazotic acid employed.

The unstable compound obtained by the action of hydrochloric acid on potassium paratolenyldioxytetrazotate becomes yellowish-white when treated with chloroform, which is caused to boil by the vigour of the action; nitric oxide is evolved in this change, but if the chloroform is artificially cooled, nitrogen is the sole gaseous product. The insoluble residue consists of paratolenylamidine paratolenyldioxytetrazotate, the filtrate containing paratoluenitrile with 10 per cent. of paratoluic acid.

The same products arise when the compound undergoes spontaneous decomposition. Under the influence of ammonia, added to the liquid in which the compound has been precipitated, it yields paratolenylamidine

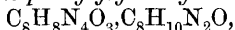
paratolenyldioxytetrazotate, but if the substance is first isolated, and then treated with dilute ammonia until the alkaline action persists, ammonium paratolenyldioxytetrazotate passes into solution, and a red compound remains undissolved. *Rubamidide*, $C_8H_9N_3O$, is the name given by the authors to this substance, which has the empirical formula of paratolenylamidine paratolenyldioxytetrazotate; it is also produced by the action of aniline, and the filtrate, on evaporation, yields paratoluic acid and ammonium paratolenyldioxytetrazotate. Rubamidide explodes somewhat violently at $60-65^\circ$, and is slowly decomposed by cold water; the solution in alcohol is red but rapidly becomes colourless, yielding paratoluenitrile. It is insoluble in ether, but yields gas when kept in contact with it, forming paratolenylamidine; alcoholic potash also liberates gas, and gives rise to toluonitrile and a small proportion of potassium dioxytetrazotate. The action of hot water converts rubamidide into toluonitrile and a small proportion of amidine paratolenyldioxytetrazotate, nitrogen being set free.

From these facts, it is clear that paratolenylamidine paratolenyldioxytetrazotate and rubamidide are distinct substances, although having the same empirical formula, which is also that of a nitroso-paratolenylamidine; it is quite possible, therefore, that rubamidide is a compound of the latter class.

M. O. F.

Phenylglycolenyldioxytetrazotic Acid and Phenylglyoxenyldioxytetrazotic Acid. By WILHELM C. LOSSEN and FRANZ BOGDAHN (*Annalen*, 1897, 297, 371—380. Compare foregoing abstracts).—*Phenylglycolenyldiamidine* (phenylhydroxyacetamidine) has been prepared by C. Beyer (*Abstr.*, 1885, 983); the *nitrate* forms rhombic or monoclinic crystals, and melts and decomposes at 154° .

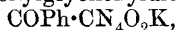
Phenylglycolenyldiamidine phenylglycolenyldioxytetrazotate,



is obtained by adding potassium nitrite solution and a small quantity of nitric acid to a warm, aqueous solution of phenylglycolenyldiamidine hydrochloride (1 mol.), the product being treated alternately with potassium nitrite and nitric acid until a molecular proportion of each has been added. It is a crystalline powder which explodes when heated; it dissolves in alcohol, but is insoluble in alcohol and ether. The *potassium* salt crystallises from water, but decomposes on boiling the solution; it is highly explosive, and detonates when heated, or rubbed, or treated with concentrated sulphuric acid. The *barium* salt crystallises in aggregates; it is less explosive than the potassium salt. The *silver* salt is amorphous and colourless; it is an explosive substance, and rapidly darkens when exposed to light. The *aniline* salt crystallises in white leaflets, but rapidly becomes brown, and acquires the odour of aniline; it explodes when heated on platinum foil.

When an aqueous solution of potassium phenylglycolenyldioxytetrazotate is boiled, nitrogen is set free, and potassium mandelate produced; hot dilute sulphuric acid liberates a mixture of nitrogen and nitric oxide, and gives rise to mandelonitrile.

The *potassium* salt of phenylglyoxenyldioxytetrazotic acid,



is obtained by oxidising potassium phenylglycolenyldioxytetrazotate

with potassium permanganate at 60° ; it crystallises in long, lustrous, white needles, which become greenish-yellow in the desiccator, and forms a greenish-yellow solution in water. The salt explodes when heated, and also on treatment with concentrated sulphuric acid; a very dilute solution (1:7000) has a sweet, astringent taste.

The *silver* salt is a yellowish-brown, amorphous compound which is highly explosive.

The potassium salt of phenylglyoxyndioxytetrazotic acid undergoes a characteristic change when the aqueous solution is boiled, yielding nitric oxide, nitrogen, benzoic acid, and hydrogen cyanide; the two last named are probably due to the intermediate production of the nitrile of benzoylformic acid. M. O. F.

β -Naphthenyldioxytetrazotic Acid. By WILHELM C. LOSSEN and GUSTAV GRABOWSKI (*Annalen*, 1897, 297, 380—385. Compare foregoing abstracts).— β -Naphthenylamidine β -naphthenyldioxytetrazotate, $C_{11}H_8N_4O_2 \cdot C_{11}H_{10}N_2$, is prepared by adding potassium nitrite (2 mols.) to aqueous β -naphthenylamidine hydrochloride (1 mol.), dissolving in water the precipitate so formed, and treating the solution with concentrated nitric acid (1 mol.); it explodes at 180° , and gives Liebermann's reaction for nitroso-compounds. The *potassium* salt crystallises from water in yellowish needles, and explodes with exceptional violence when heated, or on treatment with concentrated sulphuric acid. The *silver* salt is also explosive.

β -Naphthenylamidine, employed in the production of the foregoing salts, has been prepared by Lohmann (*Ber.*, 1878, 11, 1486), and melts at 145° ; the *nitrite* crystallises from alcohol in colourless needles and melts at 122° . The *nitrate* is also crystalline, and the *platinochloride* forms slender, yellowish needles and melts at 216 — 217° .

It is noteworthy that anisenylamidine does not give rise to a dioxytetrazotic acid. M. O. F.

Tetrazotic, Oxytetrazotic, and Dioxytetrazotic Acids. By WILHELM C. LOSSEN (*Annalen*, 1897, 298, 54—55).—A summary of the results described in the following abstracts. M. O. F.

Benzenyloxytetrazotic Acid. By WILHELM C. LOSSEN and FRIEDRICH FUCHS (*Annalen*, 1897, 298, 55—67. Compare Lossen, Abstr., 1891, 1041).—Benzenyloxytetrazotic acid separates from a mixture of ether with a small quantity of alcohol in rhombic, hemihedral crystals; $a:b:c = 0.9506:1:0.6236$. Concentrated hydrochloric acid at 160° resolves the substance into benzonitrile, benzoic acid, and ammonium chloride, whilst concentrated sulphuric acid at 185° gives rise to metasulphobenzoic acid; nitric acid (sp. gr. = 1.53) acts vigorously on the compound, producing nitrobenzoic acid.

The *calcium* salt of benzenyloxytetrazotic acid crystallises from water in cubes, containing $3H_2O$, and the *sodium* salt contains $1H_2O$; the *cobalt* salt forms large, reddish crystals containing $2H_2O$, and the *copper* salt, which contains $3H_2O$, crystallises in green, microscopic needles. The *methylic* salt is crystalline, and melts at 40° ; the *ethylic* salt is a yellowish oil, and yields benzoic acid, benzonitrile, ethylic chloride,

and ammonium chloride when heated in a sealed tube with concentrated hydrochloric acid at 160° . The *nitromethylic* salt, obtained by dissolving the methylic salt in nitric acid (sp. gr. = 1.53), crystallises from alcohol in long needles melting at 118° ; reduction with stannous chloride and hydrochloric acid converts this substance into the *amidomethylic* salt, which crystallises from hot water in slender needles, and melts at 110° ; the *hydrochloride* forms yellow plates.

M. O. F.

Paratolenyloxytetrazotic Acid. By WILHELM C. LOSSEN and PAUL SCHNEIDER (*Annalen*, 1897, 298, 67—78).—*Paratolenyloxytetrazotic acid*, $C_8H_8N_4O$, obtained by reducing paratolenyldioxytetrazotic acid with 10 per cent. sodium amalgam, crystallises from water in slender, colourless needles, and from a mixture of ether and alcohol in lustrous prisms; it contains $1H_2O$, which is removed at 120° , and melts and decomposes at 172° , yielding paratoluonitrile, nitrogen, and nitrous oxide. Concentrated hydrochloric acid at 155° resolves the compound into paratoluic and paratolenyloxytetrazotic acids, the same effect being produced by concentrated sulphuric acid at 170° ; nitric acid (sp. gr. = 1.105) gives rise to toluonitrile and paratoluic acid, the latter being also produced when paratolenyloxytetrazotic acid is heated with alcoholic ammonia at 160° . The acid, $C_8H_8N_3O$, a bye-product in the preparation of paratolenyloxytetrazotic acid, melts at 154° ; the *calcium* salt contains $3H_2O$, and the *silver* salt is somewhat soluble in ether, alcohol, and hot water.

The *potassium* salt of paratolenyloxytetrazotic acid is anhydrous, and the *sodium* salt, which crystallises from alcohol in slender needles, contains $1\frac{1}{2}H_2O$; the *barium* and *calcium* salts contain $3H_2O$, the *cobalt* salt, which separates from water in small, red crystals, $2H_2O$, whilst the *copper* and *silver* salts are anhydrous. The *ethylic* salt is a colourless liquid, yielding paratoluonitrile, paratoluic acid, and ammonium chloride when heated with hydrochloric acid at 170° ; the *methylic* salt is crystalline and melts at 44° .

M. O. F.

Phenethenyloxytetrazotic Acid. By WILHELM C. LOSSEN and ERNST KAMMER (*Annalen*, 1897, 298, 78—88).—*Phenethenyloxytetrazotic acid*, $C_8H_8N_4O$, prepared by reducing phenethenyldioxytetrazotic acid with 10 per cent. sodium amalgam, crystallises from water in concentric groups of colourless needles; it melts at 135° , and explodes at higher temperatures. Caustic potash at 250° converts the substance into phenylacetic acid, but concentrated hydrochloric acid at 155° leaves the substance for the most part unchanged, a small quantity of nitrile and ammonium chloride being produced; concentrated sulphuric acid at 180° gives rise to sulphophenylacetic acid.

The *silver* salt of phenethenyloxytetrazotic acid is a white, amorphous powder, and melts at about 73° ; the *copper* salt contains $3H_2O$. The *ammonium* salt crystallises in small, colourless needles, and melts at 145° , the *aniline* salt separates from ether in plates, and melts at 142° , and the *phenylhydrazine* salt melts at 157.5° . The *methylic* salt, which is a highly explosive, yellow liquid, yields a *nitro*-derivative when treated with nitric acid (sp. gr. = 1.53).

M. O. F.

Phenylglycolenyloxytetrazotic Acid. By WILHELM C. LOSSEN and FRANZ BOGDAHN (*Annalen*, 1897, **298**, 88—91).—*Phenylglycolenyloxytetrazotic acid*, $C_8H_8N_4O_2$, obtained by reducing phenylglycolenyldioxytetrazotic acid with 2 per cent. sodium amalgam, separates in small crystals on adding light petroleum to the alcoholic solution, and melts at 141° . The *silver* salt is white, and resists the action of light; the *barium* salt crystallises in thin leaflets, and is anhydrous.

M. O. F.

Benzenyltetrazotic Acid. By WILHELM C. LOSSEN and FRANZ STATIUS (*Annalen*, 1897, **298**, 91—105. Compare Lossen, Abstr., 1891, 1041).—Benzenyltetrazotic acid is most conveniently prepared by Pinner's method (Abstr., 1894, i, 386). The *sodium* salt crystallises in lustrous, highly refractive leaflets containing $3H_2O$, and the *calcium* salt, which forms transparent prisms, contains $4H_2O$; the *copper* salt is anhydrous, and the *ammonium* salt, which crystallises in white leaflets, undergoes dissociation when heated. The *methylic* salt separates from a mixture of alcohol and ether in transparent, prismatic crystals, and melts at 40° . When benzenyltetrazotic acid is heated alone at 218° , nitrogen is evolved, and a mixture of diphenyltriazole and diphenyltetrazine produced.

Bromobenzenyltetrazotic acid, $C_7H_5N_4Br$, is obtained by heating benzenyltetrazotic acid with bromine and water at 160° during 16 hours; it crystallises from dilute alcohol in flat, transparent prisms, and melts at 265° . *Nitrobenzenyltetrazotic acid*, $NO_2 \cdot C_7H_5N_4$, is formed when benzenyltetrazotic acid is dissolved in nitric acid (sp. gr. = 1.55) mixed with concentrated sulphuric acid; it crystallises from water, and melts at 145° . The *barium* salt contains $3H_2O$, and the *silver* salt, which is yellowish-white, resists the action of light.

M. O. F.

Paratolenyltetrazotic Acid. By WILHELM C. LOSSEN and CARL KIRSCHNICK (*Annalen*, 1897, **298**, 105—107).—Paratolenyltetrazotic acid, $C_8H_8N_4$, obtained by reducing paratolenyldioxytetrazotic acid with sodium amalgam, crystallises from alcohol in small needles, and melts at 248° . (Compare Pinner and Caro, Abstr., 1895, i, 137.)

M. O. F.

Anisenyltetrazotic Acid. By WILHELM C. LOSSEN and JAMES COLMAN (*Annalen*, 1897, **298**, 107—116).—*Anisenyltetrazotic acid*, $OMe \cdot C_6H_4 \cdot CN_4H$, which is best prepared by Pinner's method (Abstr., 1895, i, 137), crystallises from dilute alcohol in white needles melting at 228° . The *potassium* salt crystallises in long needles, and is readily soluble in water, the *ammonium* salt forms leaflets, and the *barium* salt crystallises from alcohol in thin, quadratic plates. The *methylic* salt crystallises from dilute alcohol in long needles, and melts at 93° ; the *ethylc* salt also forms long needles, and melts at 62° .

Nitroanisenyltetrazotic acid is obtained by heating anisenyltetrazotic acid with nitric acid (sp. gr. = 1.4) in boiling water for $1\frac{1}{2}$ minutes, and pouring the liquid into cold water after an interval of ten minutes; it crystallises from hot water in long, yellow needles containing $1H_2O$, and melts at 203° . The *barium* salt crystallises from water in

plates, and contains $3\text{H}_2\text{O}$. *Amidoanisenylnitrazotic acid*, prepared by reducing the nitro-acid with stannous chloride and hydrochloric acid, crystallises from hot water in needles containing $1\text{H}_2\text{O}$ and melts at 223° . The *hydrochloride* forms needles containing $1\text{H}_2\text{O}$, and the *potassium* salt crystallises in long needles containing $1\text{H}_2\text{O}$.

M. O. F.

Etherification of Mono-substituted Benzoic Acids. By VICTOR MEYER (*Zeit. physikal. Chem.*, 1897, 24, 219—220).—The author had previously stated, as a general law, that, in the case of the mono-substituted benzoic acids, the velocity of etherification is least for the ortho-acids, and that their ethereal salts are the most difficult to hydrolyse (Abstr., 1895, ii, 466). The results of Kellas' experiments (following abstract) are in complete accord with this law, and, further, indicate the marked influence of the molecular weight of the acid, in the case of compounds with analogous substituents; thus, chlorobenzoic acid is etherified more rapidly than the brominated compound, and this again more rapidly than the iodo-compound.

L. M. J.

Velocity of Etherification of Mono-substituted Benzoic Acids, and Hydrolysis of their Ethereal Salts. By ALEXANDER M. KELLAS (*Zeit. physikal. Chem.*, 1897, 24, 221—252). The researches of Meyer (Abstr., 1895, ii, 466) have shown that, in general, ortho-aromatic acids are more rapidly etherified than the corresponding meta- or para-derivatives. The author, therefore, determined the velocity of etherification for a large number of mono-substitution derivatives of benzoic acid in order to prove the general law and determine the influence of temperature, and of the nature of the substituent. The acids employed were, toluic acids, nitro-, chloro-, bromo-, iodo-, and hydroxy-benzoic acids, the three isomerides being used in each case. The effect of the position of the substituent is seen from the accompanying table, which gives the quantity of ethereal salt produced under similar conditions; the vertical sets alone being comparable.

	Cl-.	Br-.	I-.	NO_2 -.	CH_3 -.	-OH.
Ortho-.....	35.7	7.0	9.3	4.2	28.4	15.3
Meta-.....	55.2	18.4	28.3	22.3	63.8	55.9
Para-.....	53.1	17.2	26.8	22.3	71.0	51.3

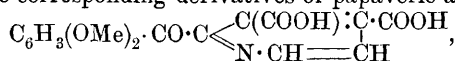
Experiments were then made at a series of temperatures varying from 0° to 51° ; the velocity was found to increase with temperature, and tables and curves are given for each acid, the curve in all cases being convex to the temperature axis and considerably steeper for the meta- and para- than for the ortho-derivatives, so that the values approach at 0° . To determine the influence of the substituent, simultaneous experiments were made with various acids, equivalent quantities being used; the order of the velocities was found to be benzoic, chlorobenzoic, toluic, bromobenzoic, iodobenzoic, nitrobenzoic

for the ortho-compounds, but toluic acid comes before chlorobenzoic acid in the meta- and para-compounds, and the nitro- before the iodo-acid in the meta-compounds; the effect of molecular weight is therefore only comparable for analogous compounds. The order of the velocities of hydrolysis were not found to be the same as, or the reverse of, those of etherification, for, although the chlorbromo- and iodo-derivatives are still in the same order, yet the velocity of hydrolysis of toluic acids is much smaller than that of the iodo-acids, whilst the velocity in the case of the nitro-acid is greater than that of the chloro-derivative. In all cases, however, the velocity is least for the ortho-acids.

L. M. J.

Hemipinic Acid, and the Isomeric Alkyl Hydrogen Papaverates. By ALFRED KIRPAL (*Monatsh.*, 1897, 18, 461—466).—The hemipinic acid of which Ostwald determined the conductivity constant (*Zeit. physikal. Chem.*, 1889, 3, 268) was in reality meta-hemipinic acid; the true acid, $C_6H_2(OMe)_2(COOH)_2$ [3 : 4 : 1 : 2], which has been prepared from opianic acid, has the conductivity constant $K = 0.110$.

Ostwald found that α -methylic hydrogen hemipinate, in which the free COOH group has COOMe on one side of it, and H on the other, has a higher conductivity constant than the β -isomeride, in which the free COOH group has on one side OMe, on the other COOMe. In the case of the corresponding derivatives of papaveric acid,



that methylic hydrogen salt which has the free COOH in the 4'-position with respect to the nitrogen has a higher constant than the isomeride, where it is in the 3'-position: contrary to expectation, the author says, for reasons which it is not easy to see. These two salts, in more concentrated solutions, have a smaller conductivity than the acid, but at a greater dilution their conductivity becomes greater than that of the acid. The same is true of β -methylic hydrogen hemipinate as compared with hemipinic acid; the α -isomeride, on the other hand, has always a smaller conductivity than the acid.

C. F. B.

Behaviour of Acetylgallic Acid and Acetyltannin with Hübl's Reagent. By CARL BOETTINGER (*Chem. Zeit.*, 1897, 21, 57).—Triacetylgallic acid and pentacetyltannin are scarcely attacked by Hübl's reagent, the former giving an iodine number from 1.2 to 2.4, the latter from 2 to 3.1. These compounds dissolve easily in chloroform, but the acetyltannin which is insoluble in a dilute aqueous solution of sodium carbonate is precipitated from its solution in chloroform by adding Hübl's reagent or alcohol. Since, however, gallic acid and tannin both give large iodine numbers, this reaction would seem to be dependent on the presence of unsubstituted hydroxyl groups. Such being the case, if the composition of gallic acid and tannin be assumed to be represented by formulæ obtained by doubling the ordinary formulæ, then the former might be expected to give a larger iodine number than the latter, which contains only five instead of six hydroxyl groups, and this is in accordance with the fact. But on

this assumption, however, pentacetyltannin would contain a carboxyl group and should be of acid character, whereas it is only slowly attacked and decomposed by dilute sodium carbonate solution. It is evident that Hübl's iodine reaction in the case of gallic acid and tannin cannot be attributed to the same cause as the similar reaction afforded by fats. E. W. W.

Diacyl Anilides. By HENRY L. WHEELER, T. E. SMITH, and C. H. WARREN (*Amer. Chem. J.*, 1897, 19, 757—766).—*Benzenesulphacetanilide*, $C_6H_5 \cdot SO_2 \cdot NPhAc$, obtained by the action of acetic anhydride on sodium benzenesulphanilide, separates from dilute solution in the form of large, colourless monoclinic plates melting at 116.5° . *Benzenesulphopropionanilide*, prepared in a similar manner, separates from alcohol in very large crystals melting at 115° . *Benzenesulphobutyranilide* crystallises in stout prisms melting at $89-90^\circ$. *Benzenesulphobenzanilide* forms long, thin, monoclinic needles melting at $114-115^\circ$.

Benzenesulph-a-naphthalide, $C_{10}H_7NHSO_2C_6H_5$, prepared by the Baumann-Schotten reaction in the usual manner, crystallises from alcohol in needles melting at $168-169^\circ$. The corresponding β -*naphthalide* crystallises in oblong plates or flattened prisms melting at 97° . *Benzenesulphobenzo-a-naphthalide* forms minute crystals melting at $193-194^\circ$, and the corresponding β -compound fine, white needles melting at $161-162^\circ$. As the group $-C \begin{smallmatrix} \nearrow H \\ \searrow O \end{smallmatrix}$ exists in the diacyl anilide, the formyl derivative of the above series has been compared crystallographically with its homologues. The results show that acetyl and propionyl derivatives of benzenesulphanilide exhibit close crystallographic analogy, the compounds being monoclinic, hemimorphic, and pyroelectric, their crystallographic axes and the angle β being similar. On the other hand, benzenesulphoformanilide is orthorhombic, and shows no analogy whatever with these compounds. Moreover, crystals of formanilide showed no analogy with those of acetanilide. A. W. C.

Natural Resins ("Überwallungsharze"). III. By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1897, 18, 481—509. Compare Abstr., 1895, i, 109).—Pinoresinol, from the resin of *Pinus laricio*, has now been obtained by crystallisation from a concentrated alcoholic solution, in large rhombic prisms [$a:b:c = 0.8689:1:0.3817$]; it melts at 122° , and is now found to have the composition $C_{19}H_{20}O_6$.

The "Überwallung" resin from pines can also be separated by ether into a soluble α - and an insoluble β -resin, present respectively to the extent of 80 and 20 per cent. The α -resin consists of the pinoresinol salts of paracoumaric and abietic acids, the first of which is present in much larger amount; it also contains a little paracoumaric acid, and some vanillaldehyde, the pinoresinol obtained from it is in all respects identical with that described above, $C_{17}H_{12}O_2(OH)_2(OMe)_2$, and yields the same diacetyl and dimethyl derivatives. A *diethyl-pinoresinol* was also obtained by acting on the potassium salt with ethylic iodide and methyl alcoholic potash; it melts at 118° . Con-

centrated nitric acid converts pinoresinol in acetic acid solution at -15° into dinitroguaiacol $\text{OH} \cdot \text{C}_6\text{H}_2(\text{OMe})(\text{NO}_2)_2$ (Herzig, Abstr., 1883, 464). Bromine, in cooled acetic acid solution, converts it into *dibromoresinol dibromide*, $\text{C}_{19}\text{H}_{18}\text{Br}_4\text{O}_6$, which melted at any temperature between 225° and 254° , and was possibly not pure.

The β -resin was purified by dissolving it in alcohol, reprecipitating with very dilute hydrochloric acid, boiling for several days with 10 per cent. alcoholic potash, precipitating with sulphuric acid, redissolving in aqueous potash, precipitating the potassium salt by the addition of solid potassium hydroxide, and decomposing it with very dilute hydrochloric acid. It forms a chocolate-brown powder, has the methyl number 56, and appears to have the composition $\text{C}_{30}\text{H}_{30}\text{O}_6(\text{OMe})_2$; its properties are those of a tannol, whence it is named *pinoresinotannol*. It yields a *benzoyl* derivative when it is treated with 10 per cent. aqueous soda and benzoic chloride, and a *methylic* derivative when it is boiled with methylic iodide and methyl alcoholic potash; it is uncertain, in both cases, whether two or three benzoyl or methyl groups enter the molecule; both the products are brown and amorphous.

The "Überwallungs" resin of the larch contains caffeic acid, vanillaldehyde, and an acid resembling ferulic acid. The resinol, separated from it by the methods used in the case of pinoresinol, is named *lariciresinol*, melts at 164° , and appears to have the composition $\text{C}_{16}\text{H}_{19}\text{O}_5$; it forms a *potassium* derivative, $\text{C}_{16}\text{H}_{17}\text{K}_2\text{O}_5 + 2\text{H}_2\text{O}$. Lariciresinol gives the methyl number 73.5—81.4, but from this it is impossible to decide whether it contains two or three methoxyl groups. When it is boiled with acetic chloride, it forms an *acetyl* derivative, melting at 159° , of which the composition could not be determined satisfactorily; when its potassium salt is boiled with excess of acetic anhydride, a substance is formed which melts at 85° , and appears to be a *triacetyl* derivative. C. F. B.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1897, 297, 271—312. Compare Abstr., 1897, i, 362, 436).—The first instance of the occurrence of a derivative of methylamine in lichens is afforded by *Sticta fuliginosa* (Dickson), which contains trimethylamine.

Erythric acid has been hitherto found only in *Rocella tinctoria* (Ach.), *R. fuciformis* (Ach.), and *Lecanora (Ochrolechia) tartarea* (L.); it occurs also in *Parmelia olivetorum* (Nyl.), and in *Evernia furfuracea* (L.), giving rise to the red coloration produced on treating the medulla of these lichens with a solution of bleaching powder.

Evernic acid, first obtained by Stenhouse from *Evernia prunastri* (L.), is only to be found in one variety of this lichen, namely, *var. vulgaris* (Körber), and does not occur in *var. thamnodes* (Flotow), which must be, therefore, regarded as a separate species (*Evernia thamnodes*). This acid has been isolated by the author from *Ramalina pollinaria* (Westr.), and *Evernia thamnodes* also contains divarictic acid, obtained by Hesse from *Evernia divaricata* (L.).

Gyalolechia aurella (Hoffm.) contains callopismic (ethylpulvic) acid, which occurs also in *Callopusma vitellinum* (Ehrh.), *Gasparrinia medians*

(Nyl.), and *Candelaria concolor* (Dickson); when the acid is heated with methylic alcohol in closed tubes at 150—160°, it yields a yellowish-green methylic salt.

Rochleder and Heldt's chrysophanic acid occurs in *Gasparrinia cirrhochroa* (Ach.), and in *Callospisma flavovirescens* (Mass.); the same substance has been described as parietin by Thompson, physciatic acid by Paternò, chrysophyscin by Lilienthal, and physcion by Hesse.

The author confirms the observation of Hesse regarding the occurrence of ramalic acid in *Ramalina pollinaria* (Westr.); barbatic acid, hitherto found only in *Usnea barbata* (L.), occurs also in *Usnea longissima* (Ach.).

The presence of usnic acid has been established in the following lichens: *Usnea longissima* (Ach.), *Ramalina polymorpha* (Ach.), *Evernia thamnodes* (Flotow), *E. prunastri* (L.) var. *vulgaris* (Körber), *E. divaricata* (L.), *Parmelia conspersa* (Ehrh.), *Placodium gypsaceum* (Sm.), and *P. chrysroleucum* (Sm.).

Squamaric acid, which occurs in *Placodium gypsaceum* (Sm.), crystallises from alcohol in rosettes of slender, white needles, melting at 262—264°; it is insoluble in water, and dissolves with difficulty in chloroform and cold alcohol. The solution in concentrated sulphuric acid is yellow, and in dilute alkalis yellowish-green, the substance being somewhat soluble in sodium carbonate; the alcoholic solution reddens litmus, and develops a deep red coloration with ferric chloride. Although it resembles psoromic acid in crystalline form, melting point, and solubility, it differs from it in its behaviour towards alkalis, which do not give rise to red salts.

Placodiolin has been isolated from *Placodium chrysroleucum* (Sm.), and crystallises from ether in long, highly lustrous prisms, or in thin plates when quickly crystallised; it melts at 154—156°. It is very soluble in chloroform, but dissolves less readily in ether, benzene, and glacial acetic acid; concentrated sulphuric acid develops a red, and alkalis a yellowish-green coloration. The alcoholic solution is feebly acidic, and does not develop colour with ferric chloride; bleaching powder has no effect on the substance.

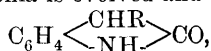
In addition to the seven species which have been mentioned in previous papers, zeorin occurs in *Anaptychia speciosa* (Wulfen), and salazinic acid, hitherto recognised in *Stereocaulon salazinum* (Bory), is present in *Alectorea cana* (Ach.), *Parmelia perforata* (Ach.), *P. excrescens* (Arnold), *P. conspersa* (Ehrh.), and *Everniopsis Trulla* (Ach.).

The presence of atranoric acid has been already established in no fewer than thirty-five species of lichens; to this number must be added the six following, *Parmelia olivetorum* (Nyl.), *P. perlata* var. *excrescens* (Arnold), *P. perforata* (Ach.), *P. Nölgherrensis* (Nyl.), *Evernia prunastri* (L.) var. *vulgaris* (Körber), *Everniopsis Trulla* (Ach., Nyl.).

Hesse's statement (Abstr., 1897, i, 257), that *Candelaria concolor* (Dickson) contains chrysophanic acid is, in the author's opinion, erroneous.
M. O. F.

Indolinones, III. By KARL BRUNNER (*Monatsh.*, 1897, 18, 527—549. Compare Abstr., 1897, i, 100, 438).—When acetic, pro-

pionic, butyric or phenylacetic hydrazide, $C_6H_5 \cdot NH \cdot NH \cdot CO \cdot CH_2R$, is heated with four times its weight of recently ignited lime for about an hour at $190-200^\circ$, ammonia is evolved and a 3'-R-2'-indolinone,



is formed, the yield varying from 70—85 per cent. of the theoretical. When $R = H$, however, it is necessary to heat to $200-220^\circ$, and the yield is only 4.5 per cent. Preliminary experiments have shown that the phenylhydrazide of isopropylacetic acid and the methylphenylhydrazide of phenylacetic acid react in the same way.

2'-Indolinone, from acetic phenylhydrazide, was found to be identical with oxindole prepared by von Baeyer's method (Abstr., 1878, 587). 3'-Methyl-2'-indolinone, from propionic phenylhydrazide, is identical with the atroxindole of Trinius (Abstr., 1885, 529); when crystallised from benzene it melts at 123° , from water at 113° , and each modification is converted into the other by contact with a crystal of the latter. When boiled with excess of acetic anhydride, it yields a *monacetyl* derivative melting at 79° ; when it is dissolved in dilute sulphuric acid and heated with excess of bromine-water, a *dibromo*-derivative, $C_6H_2Br_2 \cdot C_8NH_5O$, melting at 171° is formed; heated with methylic iodide and a methyl alcoholic solution of sodium methoxide in a sealed tube at $110-120^\circ$, a 1'-methylindolinone is not formed, but 1':3':3'-trimethyl-2'-indolinone (Abstr., 1896, i, 625, and 1897, i, 100) together with some 3':3'-dimethyl-2'-indolinone (Abstr., 1897, i, 438).

3'-Ethyl-2'-indolinone, from butyric phenylhydrazide, crystallises in monoclinic plates (fundamental angles: $100:110 = 54^\circ 10'$; $001:110 = 81^\circ 6'$; $001:011 = 51^\circ 16'$; $\beta = 74^\circ 47'$), melts at 102.5° , and boils at $200-220^\circ$ under 44 mm., at $320-323^\circ$ under 742 mm., pressure. Its *monacetyl* derivative melts at 45° ; it yields a yellow *dinitro*-derivative melting at 176° , when it is dissolved in acetic acid and the solution warmed with strong nitric acid; it also forms a *dibromo*-derivative, $C_6H_2Br_2 \cdot C_4NH_7O$, which melts at 150° . Unlike its methyl analogue, it does undergo substitution in the 1'-position when it is heated with methylic iodide and sodium methoxide in methyl alcoholic solution. 1'-Methyl-3'-ethyl-2'-indolinone boils at $280-285^\circ$ under 745 mm. pressure; it yields a *bromo*-derivative, melting at 161° , which gives up some, or all, of its bromine when boiled with alcoholic potash, and must therefore contain the bromine in the pyrrolidone, and not in the benzene, ring. 3'-Phenyl-2'-indolinone, from phenylacetic phenylhydrazide, melts at 183° ; it forms a *monacetyl* derivative, melting at 103° , and a *monobromo*-derivative, $C_6H_3Br \cdot C_8NH_7O$, melting at 191° .

C. F. B.

Action of Sulphur Chloride on Aromatic Amines. By ALBERT EDINGER (*Ber.*, 1897, 30, 2418—2420. Compare Abstr., 1897, i, 103).—The compound previously obtained by the action of sulphur chloride on quinoline has the molecular formula $C_{18}H_{10}N_2S_2$ and is very stable towards oxidising agents. Nitric acid converts it into mono- and dicarboxylic acids of pyridine, and it has therefore the constitution

$C_9NH_5 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{array} C_9NH_5$. The substance is not poisonous.

The application of this reaction to a number of aromatic amines has shown that similar compounds are only formed when the amine belongs to the quinoline series, and not when it is a derivative of pyridine, isoquinoline, or hydroxyquinoline.

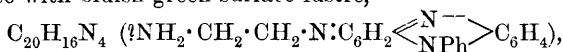
Orthomethylquinoline, when treated with sulphur monochloride or dichloride, yields a *substance* of the same composition as that obtained from quinoline itself, the methylic group being eliminated; this substance melts above 360° and is converted by nitric acid into nicotinic acid. It is accompanied by halogen derivatives of quinoline: 1:3-dichloroquinoline melting at 104°, and a tetrachloroquinoline melting at 121°. Orthohydroxyquinoline only yields a dichloro-compound melting at 179°; parahydroxyquinoline, a monochloro-compound melting at 187°, and isoquinoline, a trichloro-compound melting at 124°, no sulphur compound being formed. It has not been found possible to obtain any pure product by the application of the reaction to pyridine.

A. H.

Additive Compounds and Substitution Derivatives of Phenyltrimethylpyrazolone. By M. C. SCHUYTEN (*Chem. Zeit.*, 1897, 21, 11).—By the action of nitrous acid, that is, of a solution of sodium nitrite with glacial acetic acid, on the additive compounds of antipyrine with thiocyanic acid, cadmium chloride, zinc chloride, resorcinol, salicylic acid and chloral hydrate respectively, the bluish-green coloration characteristic of the nitroso-derivative was produced, except in the case of the resorcinol compound, which gave a yellow solution. In every case, however, more or less speedy decomposition followed and no nitroso-derivative could be isolated. From the products of the reaction with the zinc chloride compound, a yellow, flocculent precipitate which became black at 185°, and decomposed with violence at 188°, and a dark red powder were obtained. Similar negative results were obtained by passing nitric oxide gas over the above-mentioned additive compounds or their solutions. Attempts to prepare additive compounds of nitroso-antipyrine analogous to those of antipyrine also failed.

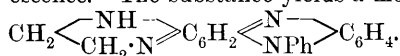
E. W. W.

Action of Bases on Aposafranine. By OTTO FISCHER and C. GIESEN (*Ber.*, 1897, 30, 2489—2494. Compare Abstr., 1896, i, 323).—By heating aposafranine hydrochloride with methylamine hydrochloride and methylamine in alcoholic solution for 5—6 hours at 100°, *methylamidosafranine*, $\text{NHMe} \cdot \text{C}_6\text{H}_2 \cdot \text{N}^--\text{NPh} \cdot \text{C}_6\text{H}_4$, is obtained; its *hydrobromide*, $\text{C}_{19}\text{H}_{16}\text{N}_4 \cdot \text{HBr}$, was analysed. Solutions of the salts are orange coloured, but are turned pink by the addition of strong acids; the iodide is only sparingly soluble. With paranisidine, green, crystalline *paranisidaoposafranine*, $\text{C}_{25}\text{H}_{20}\text{N}_4\text{O}$, is formed; solutions of this are brown; the *hydrochloride* is yellowish-green. With ethylenediamine in boiling alcoholic solution, the product is a brown, crystalline substance with bluish-green surface-lustre,



which forms orange-red solutions, coloured violet by mineral acids.

When it is heated, best with mercuric oxide, or when aposafranine is heated with ethylenediamine at 150—160°, a brownish-yellow, crystalline substance with a greenish surface-lustre is obtained; the alcoholic solution is turned first red and eventually blue by the addition of mineral acids; the solution in benzene has a greenish-yellow fluorescence. The substance yields a mon-acetyl derivative and is possibly



With orthamidophenol, aposafranine yields a brownish-red crystalline substance, possibly $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NPh} \end{array} \text{C}_6\text{H}_4$; this forms a cherry-red solution in alcohol, with a blood-red fluorescence. Naphthyl-eneorthodiamine also reacts with aposafranine. C. F. B.

A New Cyclic Compound. By MILORAD Z. JOVITSCHITSCH (*Ber.*, 1897, 30, 2426—2431).—A substance having a ring formation differing only from that of the peroxides in that it contains a nitrogen atom in place of carbon and that the two remaining nitrogen atoms are directly joined, is formed when the aniline derivative of ethylic oximidoacetate is treated with nitrous acid; that this substance is in reality represented by the formula $\text{COOEt} \cdot \text{CH} \begin{array}{c} \text{N} \text{---} \text{O} \\ | \quad | \\ \text{NPh} \text{---} \text{N} \text{---} \text{O} \end{array}$ is deduced

from the fact that of the only other two possible formulæ,

$\text{NO} \cdot \text{NPh} \cdot \text{C}(\text{NOH}) \cdot \text{COOEt}$ and $\text{NO} \cdot \text{NPh} \cdot \text{CH}(\text{NO}) \cdot \text{COOEt}$, the former is improbable, since hydroxylamine is not eliminated when the substance is heated as in Liebermann's reaction, and the latter owing to the fact that no amido-derivative is formed on reduction; the *aniline derivative of ethylic oximidoacetic acid*, $\text{NPh} \cdot \text{C}(\text{NOH}) \cdot \text{COOEt}$, is formed by the action of aniline on ethylic chloroximeacetic in alcoholic solution, and crystallises from hot dilute alcohol in long, slender prisms melting at 109°; it is nearly insoluble in cold water, but dissolves readily in alcohol and ether; the action of the calculated quantity of potassium nitrite and sulphuric acid, on an ethereal solution of this ethylic salt, gives rise to the cyclic compound above mentioned, which, after the addition of the sulphuric acid, separates from the solution in slender, orange-yellow crystals which decompose at 169°; its solution in dilute alkali is coloured deep violet, gradually changing to deep red when boiled, owing to the elimination of the carbethoxy-group and formation of the dialkali salt of the substance $\begin{array}{c} \text{CH}_2 \text{---} \text{N} \text{---} \text{O} \\ | \quad | \\ \text{NPh} \text{---} \text{N} \text{---} \text{O} \end{array}$ for which,

as also for its carbethoxy-derivative, the author does not attempt to propose a name; the free substance, which can be separated by acidifying, crystallises from dilute alcohol in slender needles containing $1\text{H}_2\text{O}$, which it loses at 140—190°, finally decomposing at 206°. The red alkali salt loses its colour on prolonged exposure to the air, and almost instantly in the presence of carbonic anhydride. A substance, $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_3$, is also formed by the action of nitrous acid on the aniline derivative; this crystallises from water in slender, yellow, fluorescent prisms melting at 69—70°. J. F. T.

Phenyltriazoles. II. By ASTRID CLEVE (*Ber.*, 1897, **30**, 2433—2438).—A continuation of a former paper in which the preparation of phenyltriazoles from Widman's 3-hydroxy-1-phenyl-1 : 2 : 4-triazoles by substitution with chlorine and subsequent reduction with hydriodic acid and red phosphorus, was described (*Abstr.*, 1897, i, 172).

3-Chloro-1-phenyl-5-propyl-1 : 2 : 4-triazole, $\begin{array}{c} \text{CCl}=\text{N} \\ | \\ \text{N}:\text{CPr}^a \end{array} > \text{NPh}$, is a tolerably mobile oil boiling at 322·5°, and having a sp. gr. = 1·1884 ; it does not yield salts with acids, but on distillation is partially converted into its *hydrochloride* which separates in glistening scales.

1-Phenyl-5-propyl-1 : 2 : 4-triazole, $\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{N}:\text{CPr}^a \end{array} > \text{NPh}$, formed from the above by reduction, is a colourless oil boiling at 285—286°, and of sp. gr. = 1·0827. The *mercuriochloride* crystallises from alcohol in colourless prisms melting at 111—112°.

3-Chloro-1-phenyl-5-butyl-1 : 2 : 4-triazole, $\begin{array}{c} \text{CCl}=\text{N} \\ | \\ \text{N}:\text{C}(\text{C}_4\text{H}_9) \end{array} > \text{NPh}$, is a pale yellow oil boiling at 327—328° (corr.), and of sp. gr. = 1·1547 ; on reduction, it yields 1-phenyl-5-butyl-1 : 2 : 4-triazole, an oil boiling at 288—289°, and yielding a *picrate* crystallising from dilute alcohol in needles melting at 136°, and a *mercuriochloride* consisting of colourless prisms melting at 116°.

3-Chloro-1-phenyl-5-phenylchlorethyl-1 : 2 : 4-triazole, $\begin{array}{c} \text{CCl}=\text{N} \\ | \\ \text{N}:\text{C}(\text{C}_2\text{H}_5\text{PhCl}) \end{array} > \text{NPh}$, which is produced when hydroxyphenylstyryltriazole is treated with phosphorus pentachloride, consists of flat needles melting at 112—113° ; on reduction, it yields 1-phenyl-5-phenylethyl-1 : 2 : 4-triazole, $\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{N}:\text{C}(\text{C}_2\text{H}_5\text{Ph}) \end{array} > \text{NPh}$, a colourless oil boiling at 340—350°, the *platinochloride* forms yellowish-red crystals decomposing at 180—190°.

1-Phenyl-5-styryl-1 : 2 : 4-triazole, $\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{N}:\text{C}(\text{CH}:\text{CHPh}) \end{array} > \text{NPh}$, prepared from phenylphenylethyltriazole by treating it with bromine, separates from a mixture of light petroleum and benzene in colourless prisms melting at 119—120°. The *hydrochloride* consists of colourless needles, the *platinochloride* of yellowish-red leaflets, whilst the *picrate* separates from alcohol in yellow prisms melting at 167°. 1-Phenyl-5-phenyldibromomethyl-1 : 2 : 4-triazole, which is an intermediate product in this reaction, forms silky needles melting at 152°. J. F. T.

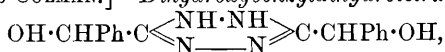
Action of Hydrazine on Imido-ethers. By ADOLF PINNER (*Annalen*, 1897, **297**, 221—271. Compare *Abstr.*, 1897, i, 637, and 1894, i, 385).—The author discusses at some length the action of hydrazine derivatives on imido-ethers. The experimental portion of the paper has been already published (*loc. cit.*). M. O. F.

Action of Hydrazine on Imido-ethers. By ADOLF PINNER (*Annalen*, 1897, **298**, 1—53. Compare foregoing abstract).—The

hydrochloride of paratolonylhydrazidine (Abstr., 1895, i, 136) forms lustrous, colourless prisms. *Tolyltetrazole* is the compound described as paratolyltetrazotic acid (*loc. cit.*), obtained by the action of nitrous acid on paratolonylhydrazidine.

[With C. GÖBEL.]—The compounds dealt with in this portion of the paper have been already described (Abstr., 1897, i, 639).

[With JAMES COLMAN.]—*Dihydroxybenzylidihydrotetrazine*,

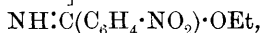


is obtained by the action of hydrazine on the imido-ether prepared from mandelonitrile, it not having been found possible to produce the intermediate hydrazidine derivative; it crystallises from alcohol in yellowish needles and melts at 193°. Hydrochloric acid resolves the substance into benzaldehyde, formic acid, and hydrazine hydrochloride. The *tetracetyl* derivative forms colourless crystals and melts at 203°.

Furfuryltetrazole is the name now given to furfuryltetrazotic acid (Abstr., 1895, i, 270).

[With ALFRED SALOMON.]—The compounds enumerated in this portion of the paper have been already described (Abstr., 1897, i, 638).

[With FELIX GRADENWITZ.]—*Paranitrobenzimidio-ether*,



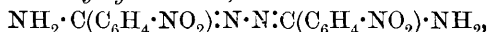
crystallises in stellar aggregates of needles and melts at 78°. The *hydrochloride* forms large, lustrous prisms and melts at 197°, yielding ethylic chloride and paranitrobenzamide; water converts it into ammonium chloride and ethylic paranitrobenzoate. The *platinochloride* crystallises in lustrous, yellow needles, and melts at 141°; the *sulphate* is unstable, and crystallises in needles.

Paranitrobenzamidine, $\text{NH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{NH}_2$, arises from the action of ammonia on the imido-ether; it crystallises in needles, and melts at 215°. The *hydrochloride* forms highly refractive, rhombic needles. *Acetoparanitrobenzamide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHAc}$, produced when the hydrochloride of the imido-ether is heated with sodium acetate and acetic anhydride, crystallises from alcohol in six-sided plates, and melts at 165°.

Paranitrobenzenylhydrazidine, $\text{NH}_2\cdot\text{N}\cdot\text{C}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is obtained by the action of hydrazine on the imido-ether, and crystallises from alcohol in lustrous, reddish needles melting at 195°. The *picrate* crystallises in yellow needles, and melts at 177°.

Paranitrophenyltetrazole, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{array}{c} \nwarrow \text{NH}\cdot\text{N} \\ \nearrow \text{N} \end{array}\text{C}$, is produced by the action of nitrous acid on the hydrazidine, and crystallises from alcohol in white needles; it melts and becomes red at 219°.

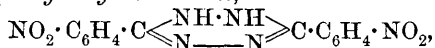
Diparanitrobenzenylhydrazidine,



is obtained by the action of alcoholic hydrazine (1 mol.) on the imido-ether ($1\frac{1}{2}$ mols.) and forms small, reddish, rhombic crystals insoluble in common solvents; it darkens at 220°, and melts at 257°. The *hydrochloride* yields diparanitrophenyltriazole when heated; the *nitrate* melts and effervesces at 143°.

Diparanitrophenyltriazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{N} \cdot \text{N} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is prepared by heating the hydrazidine with glacial acetic acid, and crystallises from alcohol in colourless needles melting at 257° . The *acetyl* derivative also forms colourless needles and melts at 237° .

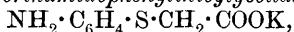
Diparanitrophenyldihydrotriazine,



is obtained from the imido-ether (1 mol.) and hydrazine ($1\frac{1}{2}$ mols.) in somewhat less concentrated solution; it forms red needles soluble in alcohol, benzene, and acetone, and melts at 215° .

Diparanitrophenyltetrazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{N} \cdot \text{N} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is produced on oxidising the foregoing compound; it crystallises in flat, red needles, and melts at 218° . M. O. F.

Action of α -Brominated Acids and Ketones on Orthamidothiophenol. By OSKAR UNGER and G. GRAFF (*Ber.*, 1897, 30, 2389—2399. Compare Abstr., 1897, i, 302).—Ketodihydrobenzoparathiazine is also formed by the action of ethylic chloracetate on amidothiophenol. When treated with aqueous potash, glistening crystals of *potassium orthamidophenylthioglycollate*,



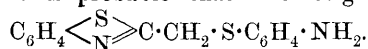
are formed. Nitrous acid yields a diazo-salt which yields a colouring matter with β -naphthol. The thiazine compound is converted by oxidation into a *compound* which melts indefinitely between 140° and 150° and yields a *phenylhydrazone*, crystallising in yellow needles and melting at 137° . When distilled with zinc dust, the thiazine yields a small quantity of indole.

α -Methylketodihydrobenzoparathiazine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \text{---} \text{CHMe} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, obtained by the action of α -bromopropionic acid on amidothiophenol, crystallises in concentrically grouped needles melting at 128° . The *ethyl* derivative is prepared by means of α -bromobutyric acid, and crystallises in porcelain white prisms melting at $105\text{--}106^\circ$, whilst *α -phenylketodihydrobenzoparathiazine*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \text{---} \text{CHPh} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, is obtained from

phenylbromacetic acid and crystallises in colourless needles melting at 204° . Ethylic α -chloracetate reacts with orthamidothiophenol to form a compound, $\text{C}_{12}\text{H}_{13}\text{NO}_2\text{S}$, which crystallises in slender, golden yellow needles and melts at 145° ; it dissolves in hydrochloric acid, yielding a solution which, on treatment with sodium nitrite, forms phenylene diazosulphide. When heated with phenylhydrazine on the water bath, it yields diamidodiphenylic bisulphide and 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone. The condensation product is completely decomposed by aqueous potash, yielding a *compound* which crystallises in colourless needles melting at 159° . Its composition has not yet been ascertained.

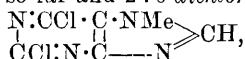
Bromacetic bromide reacts with orthamidothiophenol to form a substance of the composition $\text{C}_{14}\text{H}_{12}\text{N}_2\text{S}_2$, its molecular weight as determined by the boiling point method being about 272. It has

decided basic properties, and yields a diazo-salt with sodium nitrite. As it yields benzothiazole on oxidation with potassium permanganate, it is probable that the original compound has the constitution



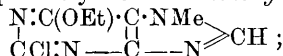
A. H.

Synthesis of Heteroxanthine and Paraxanthine. By EMIL FISCHER (*Ber.*, 1897, 30, 2400—2415. Compare *Abstr.*, 1897, i, 641, and this vol., i, 48).—Theobromine is converted by a mixture of phosphorus oxychloride and pentachloride into 7-methyltrichloropurine, but when it is heated with the oxychloride alone, the chlorination does not proceed so far and 2:6-dichloro-7-methylpurine,



is produced; this crystallises in slender, colourless needles, melting at 199—200° (corr.), and is only sparingly soluble in water. Phosphorus pentachloride at 170° converts it into trichloromethylpurine. When it is heated with hydrochloric acid (sp. gr. 1.19) at 120—125°, it yields the *hydrochloride* of 7-methylxanthine, which crystallises in almost colourless prisms. The free base $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \cdot \text{C} \end{array} \text{---N} \geq \text{CH}$, is

identical with heteroxanthine; this has no definite melting point, but softens at 360° and melts and decomposes at 380°; when quite pure, it dissolves in 142 parts of boiling water, the greater solubility found by Bondzyński and Gottlieb (*Abstr.*, 1895, i, 434) being probably due to the presence of a small amount of impurity. 2:6-Dichloro-7-methylpurine is converted by sodium ethoxide into a compound which is most probably 2-chloro-6-ethoxy-7-methylpurine,



this dissolves in about 800 parts of boiling water and crystallises in slender needles which melt and decompose at about 240°; hydrochloric acid converts it into heteroxanthine. 2-Chloro-6-oxy-7-methylpurine is obtained by warming dichloromethylpurine with an aqueous alkali and is best purified by means of the *barium* salt, which crystallises in slender prisms. The compound, which crystallises in short prisms and commences to decompose at 310°, dissolves in about 150 parts of boiling water or 250 parts of boiling alcohol. 2-Chloro-6-oxy-1:7-dimethyl-

purine, $\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CCl} \cdot \text{N} \cdot \text{C} \end{array} \text{---N} \geq \text{CH}$, is prepared by the action of aqueous

potash and methylic iodide on chloroxymethylpurine; it dissolves in about 50 parts of boiling water and melts and decomposes at about 270° when rapidly heated. 1:7-Dimethylxanthine or paraxanthine, $\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \cdot \text{C} \end{array} \text{---N} \geq \text{CH}$, obtained by heating the foregoing compound with hydrochloric acid of sp. gr. 1.19 at 125—130°, is identical with the paraxanthine isolated by Salomon from urine (*Abstr.*, 1883, 601; 1886, 266); when treated with potash and methylic iodide, it is converted into caffeine.

2-Chloro-6-oxy-7-methylpurine, on reduction with hydriodic acid, yields

6-oxy-7-methylpurine (7-methylhypoxanthine), $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{CH} : \text{N} - \text{C} - \text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH}$,

which crystallises in slender, colourless needles, melts at about 355° when rapidly heated, and is readily soluble in hydrochloric and sulphuric acids. The *nitrate* forms large, compact crystals; the *platinochloride* is readily soluble in hot water, the *aurochloride* more sparingly; the *silver* salt is a fine, white, crystalline powder. On methylation, the base yields dimethylhypoxanthine. 2-Amido-6-oxy-7-methylpurine

(7-methylguanine), $\begin{array}{c} \text{NH} - \text{CO} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{C}(\text{NH}_2) : \text{N} - \text{C} = \text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH}$, is obtained by the action

of ammonia on chloroxymethylpurine, and crystallises in slender, colourless needles which decompose at about 390° ; it readily forms crystalline salts with acids, the *hydrochloride*, *sulphate*, *nitrate*, *platinochloride* and *aurochloride* having been prepared. It also dissolves in cold dilute alkalis, but is reprecipitated by carbonic anhydride. The *sodium* salt crystallises in very slender needles, whilst the *silver* salt is an amorphous precipitate. When treated with hydrochloric acid and potassium chlorate, it yields guanidine. 2-Amido-6-oxy-1:7-dimethyl-

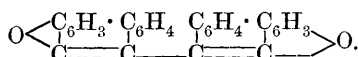
purine (1:7-dimethylguanine), $\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{NH}_2 \cdot \text{C} = \text{N} - \text{C} - \text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH}$, obtained by

the action of ammonia on chloroxydimethylpurine, separates from water in crystals which contain water of crystallisation, but become anhydrous at 100° and then melt at $343\text{--}345^{\circ}$ (corr.). The *nitrate* crystallises in plates, the *hydrochloride* and *sulphate* in needles. The *platinochloride* and *aurochloride* are both sparingly soluble. Potassium chlorate and hydrochloric acid convert it into methylguanidine.

A. H.

Non-nitrogenous Decomposition Products of Morphine. By EDUARD VONGERICHTEN (*Ber.*, 1897, 30, 2439—2444).—Bromomorphenol methyl ether, is formed when bromomethylmorphimethin-methyl iodide, is heated with concentrated sodium hydroxide solution under certain conditions, the yield being about 10 per cent. On oxidation with chromic acid, it does not yield a phenanthraquinone derivative, but is converted into a substance melting above 315° and crystallising from quinoline in glistening, reddish-brown needles having the same empirical formula as the original brominated ether. On reduction, it yields the corresponding *morphenol*, $\text{C}_{14}\text{H}_7\text{O} \cdot \text{OH}$, which crystallises from alcohol or ether in needles and melts at 135° . The *acetate* crystallises from alcohol and acetic acid in white needles.

From these and other considerations, the author considers the formula of the compound $\text{C}_{14}\text{H}_8\text{O}$ to be either $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \\ | \quad | \\ \text{CO} - \text{C} = \text{C} - \text{CO} \end{array}$ or



J. F. T.

Specific Rotatory Power of β -Glutin. By FRIEDRICH FRAMM (*Pflüger's Archiv.*, 1897, 68, 144—167).— β -glutin is strongly læv-rotatory and shows no birotation. Numerous tables are given showing the effect on the rotation of concentration, temperature, and the influence of various reagents, salts, acids, and alkalis. W. D. H.

Halogen Derivatives from Proteids. By F. GOWLAND HOPKINS and FRANCIS W. BROOK (*J. Physiol.*, 1897, **22**, 184—197).—The halogens are effective reagents for the precipitation of proteids, the present paper relating to the precipitates obtained from diluted egg white. The substances obtained, which resemble proteids in being indiffusible and of high molecular weight, give the xanthoproteic and violet biuret reactions; after gastric digestion, they give a pink biuret reaction. They are soluble in dilute alkaline solutions, from which they are precipitable by acetic acid. They differ from proteids in not giving Millon's reaction, and in being soluble in absolute alcohol; the iodine derivative is least soluble in alcohol. From their alcoholic solutions, they are precipitated by the addition of ether, the substance thus obtained containing a higher percentage of halogen than that precipitated by acid from an alkaline solution. Thus:

	Chlorine per cent.	Bromine per cent.	Iodine per cent.
Product after treatment with sodium carbonate	(3·6 and) 1·89	3·92	6·28
Product precipitated from alcoholic solution		14·89	

Taking the lower series, the bromine percentage is very nearly the mean of the chlorine and iodine percentages, in accordance with the relation that holds between the atomic weights of the halogens. It is believed that, after treatment with alkalis, one has to deal with substituted bromine, whereas after treatment with alcohol there is additive bromine as well. Since aromatic substances like tyrosine no longer give Millon's reaction when halogen has entered the ring, it seems probable that, in these derivatives of proteid, the halogen has entered an aromatic nucleus in the proteid molecule. The halogen derivatives of proteid yield no trace of lead sulphide when heated with alkaline solutions of lead salts; the sulphur is still all present, but probably in a sulphonie or other oxidised group. Efforts to obtain the original proteid from the halogen derivatives have hitherto proved fruitless.

W. D. H.

The Biuret Reaction of Albumin. By HUGO SCHIFF (*Chem. Zeit.*, 1897, **21**, 55—56).—In answer to Loew's criticism (*Chem. Zeit.*, 1896, **20**, 1000), that the anhydride of aspartic acid gives the biuret reaction, whereas, according to the author's theory, it should not do so, the author points out that the composition of this anhydride is unknown, since it is derived from 4 to 8 molecules of aspartic acid. It is characteristic, however, that aspartic acid does not give this reaction, whilst asparagine gives a reaction very similar to the biuret reaction, the coloration being only a little more bluish-violet. The product obtained by the action of formaldehyde and hydrochloric acid on albumin, which is insoluble in water and alkalis, gives the biuret reaction, for fragments of it placed in the almost colourless solution

become reddish-violet after a time. Moreover, Blum's solution of albumin (Abstr., 1896, 658), prepared by the action of formaldehyde alone, although it does not coagulate on heating, also gives this reaction. If this substance is a methylene-albumin, then, according to the author, it does not contain the symmetrical group, $\begin{smallmatrix} -\text{NH} \\ -\text{NH} \end{smallmatrix} > \text{CH}_2$, for derivatives of biuret, oxamide, and malonamide in which two hydrogen atoms of each amido-group are symmetrically substituted do not give the biuret reaction.

E. W. W.

Precipitation of Caseinogen, a Simple Means of Estimating Acidity. By PAUL GRÜTZNER (*Pflüger's Archiv.*, 1897, 68, 168—175).—When milk is added gradually to various acids, the precipitate which first forms redissolves on shaking it up. The first appearance of a permanent precipitate is a measure of the strength and acidity of the acid; the stronger acids need much more milk for this purpose, and precipitate more caseinogen than the weaker ones, thus a molecule of hydrochloric acid in dilute aqueous solution precipitates five or six times as much caseinogen as a molecule of acetic acid.

W. D. H.

Decomposition Products of Carniferrin. By PAUL BALKE (*Zeit. physiol. Chem.*, 1896, 22, 248—264. Compare Siegfried, Abstr., 1895, i, 76 and 313).—It is shown that Siegfried's carnica acid is identical with Kühne's antipeptone, considerable quantities of which the author prepared by a method differing somewhat from that described by Kühne; both compounds give similar numbers on analysis and yield identical salts. By the oxidation of barium carnate (1 equivalent) with barium permanganate (1 equivalent) at temperatures below 5°, a new acid, *oxycarnic acid*, $\text{C}_{30}\text{H}_{41}\text{N}_9\text{O}_{15}$, is obtained; it is best purified by evaporating its aqueous solution to a syrup, then pouring it into alcohol, and washing the precipitate successively with alcohol and with ether. The *zinc* salt, $\text{C}_{30}\text{H}_{39}\text{N}_9\text{O}_{15}\text{Zn}$; *barium* salt, $\text{C}_{30}\text{H}_{39}\text{N}_9\text{O}_{15}\text{Ba}$, and *silver* salt, $\text{C}_{30}\text{H}_{38}\text{N}_9\text{O}_{15}\text{Ag}_3 + 2\text{H}_2\text{O}$, are described. The *acid* itself is a snow-white, hygroscopic powder, readily soluble in water, sparingly in alcohol, and insoluble in ether. It reddens blue litmus, is capable of decomposing carbonates, and gives precipitates with picric, phosphotungstic, and tannic acids, but not with lead acetate, acetic acid, or potassium ferrocyanide.

Siegfried has shown that carniferrin obtained from milk has the same percentage composition as that obtained from meat extract, but that when hydrolysed with barium hydroxide it yields, besides lactic and succinic acids, an acid closely related to carnica acid, which he termed *orylic acid*. According to the author, orylic acid has the composition $\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}_8$. When dry, it is a yellowish-white powder, which is extremely hygroscopic and, when freshly prepared, readily soluble in water; it is sparingly soluble in alcohol but insoluble in ether, and is a strong dibasic acid, resembling carnica acid. The *zinc* salt, $\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}_8\text{Zn}$, and *silver* salt, $\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}_8\text{Ag}_3 + 3\text{H}_2\text{O}$, are described. When heated with hydrochloric acid at 130°, orylic acid yields leucine as one of its decomposition products.

J. J. S.

Organic Chemistry.

Determination of the Number of Isomeric Paraffins of the Formula C_nH_{2n+2} . By FELIX HERRMANN (*Ber.*, 1897, 30, 2423—2426).—The author describes in outline a somewhat simpler method than those adopted by Cayley and Losanitsch for the determination of the number of isomeric paraffins of the formula C_nH_{2n+2} . H. C.

Decomposition of Heptane and Octane at High Temperatures. By R. A. WORSTALL and A. W. BURWELL (*Amer. Chem. J.*, 1897, 19, 815—845).—For this investigation, ordinary crude 63° naphtha of sp. gr. = 0.7310 at 15°, consisting practically of heptane and octane, was employed; the greater portion passed over between 100° and 120°. When gas was manufactured from this material by the Pintsch process, the tar which condensed in the hydraulic main was equivalent to about 25 per cent. of the oil used; it had a sp. gr. = 0.9369 at 15°; by the action of bromine, 34.48 per cent. was added, and 18.88 per cent. substituted. It was found that 100 parts of heptane and octane yielded 25 parts of methane, 26 of olefines, 13 of acetylene, 12.5 of benzene, 3.0 of toluene, 3.0 of xylenes, &c. (120—200°), 4.5 of aromatic hydrocarbons (200—300°), 2.3 of aromatic hydrocarbons (above 300°), 3.6 of naphthalene, 1.3 of anthracene, 0.1 of phenanthrene, 0.1 of chrysene, about 0.01 of fluoranthrene (?), 0.01 of phenols. Naphthenes, thiophen, and diphenyl were absent, and no paraffins other than the original heptane and octane were present.

About 10 per cent. of a liquid was deposited during the compression of the gas under 15 to 17 atmospheres. This consisted of hydrocarbons of low boiling point, about 6 per cent. being unsaturated hydrocarbons boiling at 20—78°, 80 per cent. benzene, and 10 per cent. toluene and xylene, but no paraffins other than the original heptane and octane were present. The gas was made up of 11.8 per cent. of nitrogen, 11.3 of acetylene (and ethylene?), 15.5 of other illuminants, 18.4 of hydrogen and 42.9 of methane. 1000 cubic feet of gas was obtained from 16 gallons of oil.

It would seem, judging from these results, and those described by Letny, by Berthelot, and by Norton and Noyes, that all hydrocarbons, under similar conditions of temperature, yield the same products. If such is the case, then Schulze's theory of the formation of coal-tar hydrocarbons from phenols cannot be correct. Similarly, explanations such as those of Berthelot and Haber, which assume that the paraffins first split up into simpler molecules, are confronted by the facts that these lower hydrocarbons are not found among the products, and that hydrocarbons which do not belong to the paraffin group yield the same products as the paraffins. E. W. W.

Composition of Scottish Paraffin Oil. By FRIEDRICH HEUSLER (*Ber.* 1897, 30, 2743—2752).—The fraction boiling below 110° contains paraffins, 42 per cent.; naphthenes, 10; aromatic hydrocarbons, 7.3, and

ethylene, &c., 39; the paraffins and naphthenes were determined in the manner described below, the aromatic hydrocarbons as dinitrotoluene; the total amount of saturated hydrocarbons was also determined by boiling some of the sample for 1 hour with about 7.5 per cent. of aluminium chloride and distilling over the hydrocarbons with steam. In the case of Saxon lignite, the corresponding numbers were 16, 4, 45, and 31 per cent. The small quantity of aromatic hydrocarbons found in this may have been formed by pyrogenic reactions from the fatty hydrocarbons present, but this cannot be true of the much larger quantity contained in the Scotch oil, since only a small amount of benzene would be formed at the comparatively low temperature of the retorts in which the shale is distilled. The Scotch paraffin shale then, unlike the Saxon lignite, probably contains considerable quantities of aromatic compounds ready formed; it is, further, most probably of animal origin, whilst the lignite is vegetable.

The paraffins in the oil boiling below 180° were estimated by treating a sample with cooled fuming nitric acid, and measuring the residue; it amounted to 40—44 per cent., boiled at 149 — 154° , had sp. gr. — 0.730 at 15° , and contained C, 84.4; H, 15.8 per cent., which agrees well with C_9H_{20} . The paraffins and naphthenes were separated in company by treating the oil successively with somewhat diluted sulphuric acid, strong sulphuric acid, and fuming sulphuric acid; the residue was fractionated, and the analyses and specific gravities of the fractions showed that they contained about 20 per cent. of naphthenes. The presence of benzene, toluene, metaxylene, and cumene, and the absence of naphthalene, were also proved. Ethylene hydrocarbons were separated by adding bromine until immediate decolorisation no longer ensued; the chief fraction of the bromides formed (from the fraction of the oil boiling at 60 — 70°) boiled at 87 — 95° under 15—16 mm. pressure, had a sp. gr. = 1.623 at 15° , and contained C, 29.1; H, 4.8; Br, 66.2 (between $C_5H_{10}Br_2$ and $C_6H_{12}Br_2$, and nearer the latter). The nitriles of fatty acids were detected by boiling the oil with solid caustic potash; the solid product was separated from the oil, and dissolved in water; pyrrolines were driven off by steam-distillation, and the phenols removed after saturation with carbonic anhydride, the fatty acids being then set free with sulphuric acid. These, from a fraction of the original oil boiling at 120 — 170° , boiled at 193 — 236° , and contained C, 61.3; H, 10.1 (between $C_5H_{10}O_2$ and $C_6H_{12}O_2$ and nearer the latter). The oil also contains sulphur (0.29 and 0.23 per cent. in the fractions 130 — 140° and 170 — 180° respectively), probably in the form of thiophen derivatives.

C. F. B.

Bivalent Carbon: Chemistry of Methylene. By JOHN U. NEF (*Annalen*, 1897, 298, 202—374. Compare Abstr., 1896, i, 71).—The theoretical portion of this paper is divided into six chapters, dealing with (1) the behaviour of unsaturated compounds, (2) the dissociation of saturated into unsaturated compounds, (3) the polymerisation of unsaturated compounds, (4) the condensation law, (5) the dissociation of condensation products into their original constituents, and (6) the methylene problem.

The author recognises two classes of unsaturated substances, namely,

(A) those which contain a double or treble linking between two neighbouring atoms, as, for example, ethylene, chlorine, acetylene, oxygen, the aldehydes, ketones and fatty acids, the alkylic cyanides, $R \cdot C \equiv N$, the nitroparaffins, $O \cdot NR \cdot O$, nitric acid, $O \cdot N(OH) \cdot O$, sulphuric acid, $O \cdot S(OH)_2 \cdot O$, the alkylic cyanates, and the thiocyanates; and (B) those which contain an unsaturated atom, an atom, that is, which does not display its maximum valency, this class being typified by ammonia and the amines, methylene and its products of substitution, such as $C \cdot O$, $C \cdot N \cdot R$, $C \cdot N \cdot OH$, thio-ethers, SR_2 , alkylic chlorides, and imidogen, $:NH$. The process of saturation is not essentially different in the two classes, involving dissociation of the substances with which unsaturated compounds form additive products; the substances (C) which undergo dissociation in this way are acids, ammonia derivatives, derivatives of water and of hydrogen sulphide, halogens, hydrogen, acidic chlorides, alkylic haloids, and halogen derivatives of metals and non-metals. Members of a further group of compounds (D) are frequently dissociated with even greater readiness than those last enumerated; such are hydrocarbons, olefines, acetylene, and alky-acetylenes, compounds containing carbonyl, nitriles, nitro-compounds, methylpyridines, and methylquinolines, benzene, and the products of its substitution. It is represented that dissociation of a compound in this sense resolves it into hydrogen or halogen, and the residual complex.

The factors which determine the existence of an unsaturated substance are very numerous, and in some cases obscure, but the character and mass of radicles contained in a compound have great influence on its stability; saturation is assisted in many cases by light, heat, electrical influences, and also by the action of acids, alkalis, water, and finely divided metals. The author considers it unnecessary to regard these agencies as catalytic, attributing their influence to mechanical causes; they probably exert a dissociating influence on members of the foregoing classes, converting their components into the nascent state, in which condition they enter into combination, or undergo polymerisation. It is noteworthy that a polymeride is frequently resolved into the compound from which it is formed by the very agency which gives rise to its production.

Cases in which addition has been followed by spontaneous decomposition of the additive product have occurred with great persistence during the last few years, and the circumstance throws considerable doubt on the validity of the substitution hypothesis. It is conceivable that the process usually called substitution, in reality consists of dissociation of the radicles in which substitution is regarded as occurring, followed by addition to the substituent, the additive product being sufficiently unstable to lose spontaneously halogen hydride or water, as the case may be. The compounds which readily undergo this form of dissociation, or, in common language, the compounds which readily undergo substitution, are those comprised in class D. The readiness with which dissociation into hydrogen and hydrocarbon occurs, followed by addition to an unsaturated substance, is particularly influenced by the presence of negative radicles and atoms, and by the existence of double or treble linkings; it is also increased by those agencies, such

as light and heat, which have been already recognised as exerting a favourable influence on dissociation, polymerisation, and addition phenomena.

It is necessary to distinguish clearly between polymerisation and condensation. Polymerised products are those which arise from the combination of free valencies in the same substance, such as benzene from acetylene; condensed products, on the other hand, are formed by the addition of members of class D to the unsaturated substances of A and B. It is possible to divide the majority of the condensation processes to which carbon compounds are liable into (1) ethylene condensation, (2) carbonyl condensation, and (3) methylene condensation. The first of these groups comprises the reactions of ethylic malonate, benzylic cyanide, deoxybenzoin, ethylic cyanacetate, and malononitrile, with alkylic haloids in which the alkylic radicle is ethyl or a higher homologue; the condensation of acetaldehyde to aldol, and of ethylic acetate to ethylic sodioacetoacetate also belong to this group, which includes the Friedel-Crafts reaction of hydrocarbons with aluminium chloride and alkylic haloid in which the alkylic group is ethyl or a higher homologue. The second division embraces all condensations of benzaldehyde, in acid solution, with phenols, tertiary aromatic amines, and ethylic malonate, the production of ethylic benzoylacetate from ethylic benzoate, sodium ethoxide, and ethylic acetate, and the condensation of ethylic oxalate with ethylic acetate, acetone, acetaldehyde, and benzylic cyanide; also the condensation of acidic chlorides with benzene, of phthalic anhydride with benzene, ethylic malonate, benzylic cyanide, quinaldine, and phenol, and of carbonic anhydride with phenols and the salts of substituted acetylenes. The third group includes the production of cinnamic acid from benzaldehyde, acetic anhydride, and sodium acetate, the condensation of benzaldehyde with ketones, aldehydes, and ethereal salts under the influence of sodium ethoxide or dilute caustic soda, the condensation of ethylic formate with ethylic acetate, acetone, and acetophenone, the conversion of formaldehyde into α -acrose and β -acrose, the condensation of benzylic alcohol, benzhydrol, and aromatic hydrocarbons under the influence of concentrated sulphuric acid, and the Friedel-Crafts reaction when carried out with methylic chloride.

The behaviour of benzene towards nitric and sulphuric acids is regarded by the author as the result of the addition of the dissociated hydrocarbon to the unsaturated molecule of the acid, followed by elimination of water from the product; similarly, the conversion of the hydrocarbon into bromobenzene is traced to the addition of the dissociated molecule to the unsaturated bromine molecule, $\text{Br}:\text{Br}$, when the additive compound, $\text{HBr}:\text{BrC}_6\text{H}_5$, is produced, and spontaneously yields hydrogen bromide and bromobenzene.

It is pointed out that the same agents which induce condensation are instrumental in dissociating the product into its constituents. Ethylic acetoacetate, for instance, is resolved by sodium ethoxide into ethylic acetate, whilst mesitylic oxide, phorone, and ethylic ethylidene-malonate yield acetone, acetaldehyde, or ethylic malonate when heated with water or acids.

An investigation of numerous well-known derivatives of acetylene

has shown the author that these must be divided into two classes, (1) those derived from acetylene, $\text{CH}:\text{CH}$, usually characterised by agreeable odour and no marked chemical activity, and (2) derivatives of *acetylidene*, $\text{CH}_2:\text{C}$, which are poisonous, have an intensely disagreeable odour, are in some cases spontaneously inflammable, and generally exhibit great chemical activity. Behrend's di-iodoacetylene, Sabanéeff's monobromacetylene, and Wallach's monochloroacetylene are regarded as members of the latter class, and are referred to as *di-iodoacetylidene*, *monobromoacetylidene*, and *monochloroacetylidene*, respectively. It is probable, also, that the metallic derivatives of acetylene belong to this group.

The experimental part of the paper comprises three divisions, which deal respectively with (I) reactions of nascent diphenylmethylenes and phenylmethylenes, (II) reactions of benzaldehyde, nascent hydroxyphenylmethylenes and acetoxyphenylmethylenes, and (III) the chemistry of acetylidenes.

I.—According to Friedel and Balsohn, diphenylmethylic bromide yields benzhydrol and benzhydrol ether when heated with water. The author finds, however, that treatment with cold water during two weeks completely resolves diphenylmethylic bromide into hydrogen bromide and benzhydrol, whilst benzhydrol ether is formed on heating the bromide with 5 parts of water for 2 days on the water bath, if the hydrobromic acid is neutralised with alkali. It has been represented by Zincke and Thörner that benzhydrol ether has the constitution expressed by the formula $\begin{matrix} \text{CPh}_2 \\ | \\ \text{CPh}_2 \end{matrix} > \text{O}$, because it is produced when

benzhydrol is heated at its boiling point for sometime; from the following facts, however, it is necessary to regard the substance as a true ether of the formula $(\text{CHPh}_2)_2\text{O}$. Benzhydrol ether yields benzhydrol acetate (2 mols.) when treated with a mixture of cold glacial acetic (9 parts) and concentrated sulphuric (2 parts) acids: alcohol (10 parts) and concentrated sulphuric acid (2 parts) convert it, when gently heated, into benzhydrol ethyl ether: the solution in benzene is converted by concentrated sulphuric acid or by phosphoric anhydride into triphenylmethane. Moreover, the two expressions differ from one another by two atoms of hydrogen, and it has been shown by Klinger and Lonnes (Abstr., 1896, i, 687) that benzhydrol ether has the empirical formula $\text{C}_{26}\text{H}_{22}\text{O}$.

When benzhydrol ether is distilled rapidly under atmospheric pressure, it undergoes dissociation into diphenylmethylenes and water, which associate in part on cooling; slow distillation gives rise to benzophenone and diphenylmethane, a small quantity of benzhydrol ether being found in the distillate. This observation is not in agreement with Linnemann's statement. Benzhydrol ether, however, boils at 267° under a pressure of 15 mm., without decomposing.

On heating benzhydrol or benzhydrol ether in a distillation flask, either alone or in an atmosphere of carbonic anhydride, water is eliminated, and after 3—5 hours, the products consist principally of benzophenone and tetraphenylethane, along with a small proportion of diphenylmethane. The changes involved are regarded by the author as taking place on the following lines. Benzhydrol is first dissociated into diphenylmethylenes and water, just as formic acid yields carbon monoxide and water when heated at 167° ; the methylene derivative

then unites with the benzhydrol which is in excess, yielding benzhydrol ether. The latter slowly dissociates at 300° into diphenylmethylenes (2 mols.) and water, which reunite to form benzophenone, with liberation of hydrogen; the decomposition of water by nascent diphenylmethylenes, 2CPh_2 , is attributed to the great affinity for oxygen which bivalent carbon exhibits. If water is in part removed from the sphere of action, diphenylmethylenes undergoes polymerisation, yielding tetraphenylethylene, which is reduced by the nascent hydrogen; but if water is not removed, no trace of tetraphenylethane is produced, and the benzhydrol ether undergoes reduction, yielding diphenylmethane.

The same intermediate product, diphenylmethylenes, is formed when benzoic acid is dissociated at $180\text{--}200^{\circ}$; as in the foregoing case, it decomposes the water which is present, yielding benzophenone, whilst the hydrogen thus liberated reduces unchanged benzoic acid to diphenylacetic acid (compare Klinger and Standke, *Abstr.*, 1889, 885). To the production of diphenylmethylenes may also be attributed the formation of tetraphenylethylene and tetraphenylethane when benzhydrol acetate and benzhydrol benzoate are heated at 300° .

The uniform production of resinous polymerides which attends the treatment of benzylic derivatives with such agents as zinc dust or concentrated sulphuric acid, is attributed to the intermediate liberation of phenylmethylenes, which then undergoes polymerisation. Thus zinc dust eliminates halogen hydride from benzylic bromide and benzylic chloride at 120° , the copper-zinc couple producing this effect on the former substance at ordinary temperatures, and in each case a dark-yellow resin of the formula $(\text{C}_7\text{H}_6)_n$ is produced; if, however, the halogen derivative is dissolved in an indifferent medium, the action is much milder, and the products are toluene and dibenzyl. This difference in behaviour is regarded as being due to the fact that, in the first case, a large proportion of phenylmethylenes molecules are set free simultaneously, and then undergo polymerisation to complex molecules; on the other hand, dilution with an indifferent medium renders the dissociation much more gradual, and gives rise to polymerides of much smaller molecular weight.

The same observations apply to derivatives of benzhydrol and benzylic alcohol. Benzhydrol, benzhydrol ether, benzhydrol ethyl ether, benzhydrol acetate, and benzhydrol benzoate are all converted into red polymerides of diphenylmethylenes under the influence of aluminium chloride, phosphoric anhydride, and concentrated sulphuric acid. The effect of introducing a diluent which is not an indifferent substance is similar to that produced in the Friedel-Crafts reaction, which meets with explanation on the dissociation basis developed in the paper. For instance, triphenylmethane is produced from a mixture of benzhydrol and benzene under the influence of phosphoric anhydride or concentrated sulphuric acid, and the hydrocarbon is also obtained from a solution of benzhydrol ether or benzhydrol acetate in benzene.

Friedel and Balsohn have observed that, whilst alcoholic ammonia converts diphenylmethylic bromide into benzhydrol ethyl ether, the aqueous base gives rise to benzhydrylamine, $\text{CHPh}_2\cdot\text{NH}_2$, and dibenzhydrylamine, $\text{NH}(\text{CHPh}_2)_2$. This is explained on the assumption that diphenylmethylenes takes up alcohol more readily than ammonia,

and ammonia more readily than water, and it is pointed out that the preference of unsaturated compounds for alcohol before water has been already exhibited in the cases of ethylic cyanimidocarbonate (Abstr., 1896, i, 72), cyanogen chloride, and cyanogen bromide. Although benzylic chloride yields benzyl ethyl ether under the influence of alcoholic potash, orthonitro- and paranitro-benzylic chlorides give rise to the corresponding stilbene derivatives in quantitative amount; similarly, chloro-benzylic cyanide and bromobenzylic cyanide are converted into dicyano-stilbene. The behaviour of ethylic bromocyanacetate is, however, more remarkable.

Ethylic bromocyanacetate, $\text{CN}\cdot\text{CHBr}\cdot\text{COOEt}$, obtained by treating ethylic cyanacetate with bromine (1 mol.) at 150° , boils at 116° under a pressure of 25 mm. When dissolved in ether, and treated with metallic sodium, ethylic sodioacetate, ethylic sodiocyanacetate, or aniline, it is converted exclusively into *ethylic dicyanofumarate*, $\text{COOEt}\cdot\text{C}(\text{CN})\text{:C}(\text{CN})\cdot\text{COOEt}$, which crystallises from benzene or alcohol in colourless needles, and melts at 122° . The substances enumerated may be regarded as dissociating ethylic bromocyanacetate into hydrogen bromide and ethylic cyanomethylenecarboxylate, $\text{COOEt}\cdot\text{C}(\text{CN})\text{:}$, which then undergoes polymerisation.

Ethylic bromomalonate, on the other hand, yields exclusively ethylic ethanetetracarboxylate, $(\text{COOEt})_2\text{CH}\cdot\text{CH}(\text{COOEt})_2$, when treated with ethylic sodiomalonate in absolute ether, no trace of the ethylene-tetracarboxylate, $(\text{COOEt})_2\text{C}\text{:C}(\text{COOEt})_2$, being produced. This may be due to the initial dissociation of ethylic bromomalonate into hydrogen bromide and the methylenic derivative, $\text{:C}(\text{COOEt})_2$, which then unites with ethylic malonate, set free from the sodium derivative by the halogen hydride. The behaviour of ethylic malonate towards unsaturated compounds gives some support to this view; for instance, Claisen has shown that ethylic ethylidenemalonate yields ethylic ethylenedimalonate when heated with ethylic malonate at 200° , and by the action of benzylic cyanide on phthalic anhydride, Gabriel obtained the compound, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{C}(\text{CPh}\cdot\text{CN}) \end{smallmatrix} \text{O}$.

The foregoing facts have led the author to modify the views which have been previously expressed regarding the action of alkylic haloids on such compounds as ethylic sodiomalonate (Abstr., 1892, 140; 1893, i, 628). Instead of assuming that halogen hydride is first liberated, and that no direct displacement of sodium takes place (*loc. cit.*), the following explanation is put forward. When ethylic malonate is converted into ethylic methylmalonate by the action of methylic iodide on ethylic sodiomalonate, the alkylic iodide undergoes dissociation into methylene and hydrogen iodide, the latter removing the metal from ethylic sodiomalonate; the ethylic malonate which is thus liberated is then free to take up methylene, yielding ethylic methylmalonate. Support is lent to this view by the fact that ethylic ethylmalonate is readily produced from ethylic malonate and ethylic iodide and zinc, which also induces the introduction of two ethylic groups; it is more probable that the metal dissociates ethylic iodide into hydrogen iodide and ethylene, which is then absorbed by the ethereal salt, than that a zinc derivative of ethylic malonate is formed as an intermediate product. It is noteworthy that, whilst treatment of ethylic malonate with ethylic

iodide (1 mol.) and sodium ethoxide gives rise to a mixture of ethylic ethylmalonate and ethylic diethylmalonate in which the former preponderates, and ethylic ethylcyanacetate is produced in greater quantity than ethylic diethylcyanacetate when sodium ethoxide and ethylic iodide (1 mol.) act on ethylic cyanacetate, treatment of the last-named substance, on the other hand, with benzylic chloride (1 mol.) and sodium ethoxide yields more ethylic dibenzylcyanacetate than ethylic benzylcyanacetate. The author explains this phenomenon by attributing to ethylic malonate a greater capacity for dissociation than that exhibited by ethylic ethylmalonate, whilst ethylic benzylcyanacetate is regarded as undergoing dissociation with greater readiness than ethylic cyanacetate. On these lines, it is possible to account for the fact that ethylic ethylmalonate does not condense with acetaldehyde and benzaldehyde, differing in this respect from ethylic malonate.

It is probable also that the behaviour of benzylic cyanide and of deoxybenzoin towards alkylic haloids in presence of sodium ethoxide depends on the dissociation of the haloid into halogen hydride and alkylene, which is then absorbed by the benzylic cyanide and deoxybenzoin respectively. The same principle may be applied to the reactions of benzylic cyanide, ethylic malonate, ethylic cyanacetate, deoxybenzoin, and primary and secondary nitroparaffins, with nitrous acid, amylic nitrite, and phenyldiazonium chloride. The production of amines from ammonia and alkylic haloids may be also brought into this category.

Reverting to the action of metals on alkylic haloids, which has been investigated by Frankland, Würtz, and Fittig, the author points out that his hypothesis gains support from the fact that, in most cases, the product consists of a mixture of hydrocarbons. For instance, when sodium acts on methylic iodide in ether at 100°, methane, ethane, and ethylene are produced. This is readily explained on the assumption that methylic iodide is first dissociated into methylene and hydrogen iodide, which yields nascent hydrogen by the action of the metal, in quantity insufficient to convert the methylene entirely into methane; a part, therefore, becomes partly hydrogenised to methyl, which polymerises, a small proportion, however, escaping reduction and undergoing polymerisation, yields ethylene. As regards the mechanism of Fittig's synthesis of benzene homologues, it is maintained that when a halogen derivative of benzene is treated with methylic iodide and sodium, the benzene compound dissociates into hexacarbon tetrahydride, C_6H_4 , and halogen hydride, whilst the methylic iodide yields methylene and halogen hydride. The metal liberates nascent hydrogen from the latter in quantity insufficient (in the absence of water) to reduce the unsaturated products further than phenyl and methyl respectively; they therefore unite, forming toluene.

II.—In an alcoholic solution of ethylenic dibromide, the latter may be regarded as existing in two conditions of dissociation, namely, ethylene and bromine, or vinylic bromide and hydrogen bromide; according as zinc dust or alkali is present, either of these conditions asserts itself. The author claims to have shown that ethylidene dihydroxide, $CHMe \cdot CH(OH)_2$, may undergo dissociation in three directions, represented by vinylic alcohol, $CH_2 \cdot CH \cdot OH$, acetaldehyde, $CHMe \cdot O$, and hydroxyethylidene, $:CMe \cdot OH$; β -propylidene dihydr-

oxide, however, exhibits only two-fold dissociation into acetone and β -hydroxypropylene, $\text{CH}_3\text{:CMe}\cdot\text{OH}$, ω -dihydroxytoluene into $\text{CHPh}\cdot\text{O}$ and $\text{:CPh}\cdot\text{OH}$, whilst orthacetic acid, $\text{CMe}(\text{OH})_3$, is resolved into acetic acid, or dihydroxyethylene, $\text{CH}_2\text{:C}(\text{OH})_2$. Chloral hydrate, however, undergoes four-fold dissociation, into (1) chloral and water, (2) hydroxytrichlorethylidene, $\text{CCl}_3\text{:C}(\text{OH})_2$, (3) dichloracetylidene hydroxide, $\text{CCl}_2\text{:C}(\text{OH})_2$, and hydrogen chloride, and (4) chloroform and dihydroxymethylene, $\text{:C}(\text{OH})_2$.

Benzylidene diacetate, $\text{CHPh}(\text{OAc})_2$, is prepared by heating benzaldehyde with equal weights of acetic anhydride and glacial acetic acid in a reflux apparatus at $150\text{--}180^\circ$ for a short time, and submitting the product to distillation under a pressure of 20–30 mm.; it melts at 46° , and boils at 154° under a pressure of 20 mm. It is noteworthy that the compound is not produced by the action of acetic anhydride on benzaldehyde when the former is free from acetic acid; moreover, the anhydride prohibits the dissociation which benzylidene diacetate undergoes when exposed to the air during a prolonged period. A boiling solution of caustic soda acts very slowly on the substance, which is converted into cinnamic acid when heated with sodium acetate, either alone or in presence of glacial acetic acid; cold concentrated sulphuric or nitric acid resolves it into benzaldehyde and acetic acid.

The production of benzylidene diacetate is explained by assuming that benzaldehyde first forms with acetic acid the additive compound $\text{OH}\cdot\text{CHPh}\cdot\text{OAc}$, which dissociates into acetic acid and nascent benzaldehyde; the latter then dissociates acetic anhydride, producing benzylidene diacetate by addition.

Benzoic acetic peroxide, $\text{AcO}\cdot\text{OBz}$, is obtained by exposing a mixture of benzaldehyde and acetic anhydride (2 mols.) to the air until the liquid is free from aldehyde; in diffused light, this effect is produced in 43 days, exposure to sunlight for 20–25 days being generally sufficient. The oily product is agitated with 2–3 parts of cold concentrated nitric acid, which resolves benzoic acetic oxide into benzoic and acetic acids, and converts benzylidene diacetate into acetic acid and benzaldehyde; the liquid is then poured into water, extracted with ether, and the ethereal extract agitated with caustic soda, dried, and evaporated, the product being treated once more with concentrated nitric acid. It crystallises in colourless, transparent needles, and melts at $37\text{--}39^\circ$, exploding with considerable violence at $85\text{--}100^\circ$. It is possible to avoid the simultaneous production of benzoic acetic oxide by exposing benzaldehyde and acetic anhydride (1 part) mixed with sand (20 parts) to diffused daylight for 4 days in porcelain basins; the mass is extracted with ether, and the extract washed with sodium carbonate.

Benzoic acetic peroxide has a marked odour of ozone, decolorises a solution of indigo-sulphuric acid, and liberates iodine from potassium iodide. Cold dilute caustic soda slowly converts it into benzoic acid, sodium peroxide, oxygen, and benzoic peroxide, whilst sodium carbonate, although acting more slowly, gives rise to a greater proportion of benzoic peroxide; it sets free chlorine from concentrated hydrochloric acid, and is decomposed by concentrated sulphuric acid in an explosive manner. Its behaviour in general appears to indicate a tendency to dissociate into benzoic acetic oxide and ozone.

Metanitrobenzoic acetic peroxide, $\text{AcO}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is prepared by dissolving benzoic acetic peroxide in fuming nitric acid and pouring the liquid into water after an interval of 15 minutes; it crystallises from methylic alcohol in colourless needles, and melts at 68° .

Acetic peroxide $\text{AcO}\cdot\text{OAc}$, was first obtained by Brodie from barium peroxide and acetic anhydride, as an oil. It is more conveniently prepared by mixing hydrogen peroxide with acetic anhydride (2 mols.) at -10° , allowing the liquid to remain below 30° during 6 hours, diluting with ether, and then agitating with a 10 per cent. solution of sodium carbonate; the ethereal portion is dried and carefully evaporated, the residue being distilled with extreme caution under reduced pressure. Acetic peroxide forms transparent crystals and melts at 30° ; it boils at 63° under a pressure of 21 mm., and explodes with great violence when heated above 100° , or on vigorous agitation. The odour is indistinguishable from that of ozone, and it probably owes its oxidising and explosive character to ready dissociability into that substance and acetic anhydride; if kept in loosely closed vessels, it is completely converted into acetic anhydride and acetic acid at the end of four months, and treatment with caustic soda rapidly yields acetic acid and sodium peroxide. Berthelot's ethylic peroxide, obtained by the action of ozone on ether, consists principally of acetic peroxide (compare also Vanino and Thiele, *Abstr.*, 1896, i, 597).

Diphenylformal peroxide hydrate, $\text{O}_2(\text{CHPh}\cdot\text{OH})_2$, is obtained by treating benzaldehyde (10 grams) with hydrogen peroxide (3 grams) in three portions, the temperature of the liquid being maintained below 30° ; it melts at $60\text{--}62^\circ$, and is insoluble in cold ether and petroleum. Both in the solid state and when treated with sodium carbonate, it is dissociated into benzaldehyde and hydrogen peroxide without the formation of benzoic acid; cold acetic anhydride converts it into acetic peroxide, acetic acid, and benzaldehyde.

Ozone, acetic peroxide, and benzoic acetic peroxide have all the same odour, which is due either to atomic oxygen produced by their dissociation, or to the ozone formed from ordinary oxygen under the oxidising influence of atomic oxygen. The readiness with which the acidic derivatives of hydrogen peroxide dissociate into oxides and atomic oxygen suggests similar behaviour on the part of hydrogen peroxide itself, which would yield water and atomic oxygen; but it is well known that the substance dissociates also into nascent hydrogen and molecular oxygen, and this double dissociation affords an explanation of the simultaneously reducing and oxidising character of hydrogen peroxide. From this point of view, slow combustion in presence of water may be regarded as taking place in the following stages: (1) decomposition of water by the combustible material, (2) conversion of atmospheric oxygen into hydrogen peroxide by the nascent hydrogen produced, (3) dissociation of hydrogen peroxide into water and atomic oxygen, which then exerts direct oxidising action. Atmospheric oxygen never undergoes direct absorption.

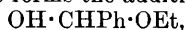
Just as zinc, iron, lead, and phosphorus become oxidised at much lower temperatures in presence of caustic soda than when oxygen and water alone are present, so benzaldehyde, under the influence of caustic alkali, yields hydrogen, benzylic alcohol, and benzoic acid. This probably

depends on initial production of ω -dihydroxytoluene, which undergoes dissociation into phenylhydroxymethylene; the hydrogen liberated by the action of the latter substance on water reduces a portion of the aldehyde to benzylic alcohol, whilst the phenylhydroxymethylene takes up hydroxyl, the product becoming dissociated into benzoic acid and water. Similarly, formaldehyde yields methylic alcohol and formic acid. In this connection, the author emphasises the enormous importance of water in oxidation phenomena. The oxidation of aldehydes, ketonic alcohols, aldehydic alcohols, and members of the sugar group, depends, broadly speaking, on dissociation into a methylene derivative, which liberates nascent hydrogen from the water present; the nascent hydrogen then reduces the oxidising agent. In the same way is explained the production of formic and acetic acids along with alkali nitrite from nitroglycerol under the influence of alkalis, the formation of hydrogen along with formic and acetic acids on heating glycerol with solid potash, and the violently explosive character of nitroglycerol and methylic nitrate.

Amongst numerous cases with which the author illustrates his hypothesis is the phenomenon of fermentation. Organised ferments, or the enzymes which constitute their active principle, are regarded as capable of inducing dissociation of the sugar molecule; the methylene derivative thus produced decomposes water, setting free nascent hydrogen. Although, theoretically, a molecule of glucose is capable of dissociating in many different ways, a directive influence is exerted by the ferment, just as the dissociation of ethylenic dibromide is controlled by zinc dust or alkali.

Although phenylhydroxymethylene is capable of decomposing water and alcohol, these substances are not attacked if compounds are present which undergo dissociation more readily; such are acetaldehyde, acetone, acetophenone, ethylic acetate, benzylic cyanide, and ethylic malonate. It has been shown that benzylidene diacetate yields cinnamic acid when heated with sodium acetate at 180° , and it is on the intermediate formation of the first-named substance that the production of cinnamic acid from benzaldehyde, acetic anhydride, and sodium acetate depends. Benzylidene diacetate is dissociated by sodium acetate into phenylacetoxymethylene, to which acetic acid then adds itself; elimination of acetic acid from the product gives rise to cinnamic acid. It is shown experimentally that nascent benzaldehyde is not capable of adding acetic acid or the anhydride, and the synthesis in question is therefore ascribed to phenylacetoxymethylene; it cannot, however, be settled definitely whether it is acetic acid, sodium acetate or acetic anhydride which unites with the nascent phenylacetoxymethylene.

The conversion of benzaldehyde into benzoin is traced as follows. Alcohol with benzaldehyde forms the additive compound,



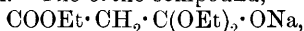
which, under the influence of potassium cyanide, is dissociated into alcohol and phenylhydroxymethylene; the later polymerises to the ethylene derivative, $\text{OH} \cdot \text{CPh} : \text{CPh} \cdot \text{OH}$, to which alcohol is added and then eliminated from the product, yielding benzoin. The deleterious effect of sodium ethoxide is due to the fact that the additive compound

of benzoin and alcohol, $\text{OEt} \cdot \text{CPh}(\text{OH}) \cdot \text{CHPh} \cdot \text{OH}$, yields benzaldehyde under the influence of that substance.

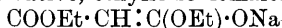
Benzaldehyde owes its conversion into hydrobenzamide, in the first place, to the production of the additive compound, $\text{OH} \cdot \text{CHPh} \cdot \text{NH}_2$; this undergoes dissociation into water and phenylamidomethylene, which polymerises to diamidostilbene, the latter becoming added to benzaldehyde, and yielding hydrobenzamide.

In the condensation of acetaldehyde to aldol by means of acids and alkalis, the author recognises vinylic alcohol as an intermediate product. An aqueous solution of acetaldehyde may be regarded as containing ethylidene dihydroxide, $\text{CHMe}(\text{OH})_2$, which, on elimination of water, becomes dissociated into three products, acetaldehyde, hydroxyethylidene, and vinylic alcohol; the last-named substance then undergoes ethylene condensation with ethylidene dihydroxide, yielding aldol and water. The *basic mercury* derivative of vinylic alcohol, $(\text{C}_2\text{H}_3\text{O})_2\text{Hg} \cdot \text{HgO}$, is produced when an aqueous solution of acetaldehyde is added to freshly precipitated mercuric oxide, and agitated with sodium carbonate or caustic soda; it is a white powder which gradually decomposes in the desiccator, yielding acetaldehyde, which is immediately produced under the influence of dilute hydrochloric or sulphuric acid. The action of acetic and benzoic chlorides is very vigorous, and bromine converts it into substitution products of acetaldehyde.

The formation of ethylic acetoacetate, and of condensation products of acetone with acids and ammonia, must be also regarded as due to ethylene condensation. The ortho-compound,



obtained from ethylic malonate and sodium ethoxide, loses alcohol and yields the ethylene derivative, ethylic sodiomalonate,



(compare Abstr., 1892, 140). Similarly, from ethylic acetate and sodium ethoxide, arises the ethylene derivative, $\text{CH}_2 : \text{C}(\text{OEt}) \cdot \text{ONa}$, which is incapable of free existence, and therefore unites with ethylic acetate, acetone, or acetophenone, forming the sodium derivative of ethylic acetoacetate, acetylacetone, or benzoylacetone respectively.

It has been now for many years generally accepted that the production of ether from alcohol and concentrated sulphuric acid at 140° depends on the initial production of ethyl hydrogen sulphate, which undergoes double decomposition with a second molecule of alcohol, yielding ether and sulphuric acid. The author, however, prefers to regard the change as involving dissociation of ethyl hydrogen sulphate into sulphuric acid and nascent ethylene, which is then absorbed by the alcohol present; the production of ether from ethylic iodide and sodium ethoxide is explained on similar lines. The presence of nascent ethylene harmonises with the formation of large quantities of ethylic chloride when ethylic alcohol is treated with sulphuric acid and sodium chloride, although very little is produced when alcohol is heated with hydrogen chloride; moreover, whilst it is possible to actually separate methylic alcohol and concentrated nitric acid by distillation, the presence of concentrated sulphuric acid at once gives rise to methylic nitrate, owing to the dissociation of the methyl hydrogen sulphate into methylene, which then unites with nitric acid.

The slow combustion of dry ether to acetaldehyde, acetic acid, and hydrogen peroxide, the production of ethylic peroxide under the influence of ozone, and the recognition of divinyl ether as a product of spontaneous decomposition, now meet with analogous explanation. With regard to divinyl ether, which was supposed by Poleck and Thümmel to be vinylic alcohol (Abstr., 1890, 118), it must be mentioned that its identity is not fully established; as, however, a solution of mercuric chloride in hydrogen potassium carbonate yields no precipitate, it cannot be vinylic alcohol. The production of formaldehyde and formic acid along with hydrogen peroxide, acetaldehyde, and acetic acid (Legler, Abstr., 1886, 327), when the combustion of ether is effected at 260—500°, depends on the formation of ethylene, which is dissociated into methylene; the latter burns to hydrogen peroxide and dihydroxymethylene, which further oxidation converts into orthoformic acid. The compound, $(C_2H_6O_4)_3$, obtained by Legler, arises from formaldehyde and hydrogen peroxide, and is therefore regarded as formal peroxide hydrate, $O_2(CH_2 \cdot OH)_2$. The exclusive production of formaldehyde when ethylene is burnt in oxygen at 400° is also explained on the assumption that the hydrocarbon is dissociated into methylene.

In this connection, the author describes an attempt to produce free methylene. Methylenic iodide is slowly converted into formaldehyde when heated with mercury in air at 100°, and the same product is formed on heating the methylene additive compounds, $CH_2 \cdot HgI_2$ and $CH_2 \cdot Hg_2I_2$, in air. If, however, the operation is carried out in an atmosphere of nitrogen at 180°, ethylene is the sole product. Methylene is probably liberated, and, in the absence of an oxidising agent, undergoes polymerisation.

It is well known that the slow oxidation of animal and vegetable matter, and many carbon compounds, is associated with the production of hydrogen peroxide and active oxygen, and is also accompanied by phosphorescence phenomena (Radziszewski, Abstr., 1881, 488). It has been already pointed out that the two-fold dissociation of hydrogen peroxide can give rise to both atomic oxygen and hydrogen, and the author maintains that the phosphorescence phenomena are due to the formation of methylene by dissociation of the organic matter, the hydrocarbon undergoing combustion in moist air in a manner resembling the ignition of phosphorus and other spontaneously inflammable substances.

III.—Tetrabromomethylene, $CBr_2 \cdot CBr_2$, is obtained by adding bromine (3 mols.) to silver acetylide suspended in water, the liquid being continuously agitated meanwhile; it melts at 56°, and boils at 100°, 104°, and 109°, under pressures of 15 mm., 20 mm., and 25 mm., respectively.

Asymmetric dibromovinyl ether, $CBr_2 \cdot CH \cdot OEt$, is prepared by heating tetrabromomethylene with alcohol in which sodium (4 mols.) has been dissolved; the product may be separated into two fractions, the portion boiling at 72—73° under a pressure of 33 mm. consisting of ethylic bromacetate and dibromovinyl ether. On treating the mixture with ammonia, ethylic bromacetate is converted into bromacetamide, leaving dibromovinyl ether undissolved; the latter boils at 75—76°.

under a pressure of 30 mm. Concentrated nitric acid converts dibromovinyl ether into ethylic dibromacetate. Cold alcoholic sodium ethoxide (1 mol.) gives rise to ethylic bromacetate, but ethylic ethoxyacetate is produced with excess of the agent.

Asymmetric dibromovinyl ether is identical with the dibromovinyl ether obtained by Sabanéeff from acetylene dibromide and alcoholic potash; its production from tetrabromomethylene is explained by assuming its dissociation into bromine and dibromacetylidene, $\text{CBr}_2:\text{C}$, which takes up alcohol. Acetylene dibromide, on the other hand, is dissociated in two directions, (1) into hydrogen bromide and bromacetylidene, $\text{CHBr}:\text{C}$, and (2) into acetylene and free bromine, which immediately unites with bromacetylidene, forming tribromomethylene, $\text{CHBr}:\text{CBr}_2$; the latter is dissociated by alkali into hydrogen bromide and dibromacetylidene, which takes up alcohol, yielding dibromovinyl ether.

Di-iodacetylidene, $\text{CI}_2:\text{C}$, prepared by treating tetriodethylene with alcoholic sodium ethoxide (2 mols.), crystallises from petroleum in needles melting at 81° ; it is also produced by the action of sunlight on tetriodethylene, and by the action of iodine on silver acetylide suspended in ether. The substance has been hitherto regarded as di-iodacetylene, $\text{CI}:\text{CI}$, and is also formed when alcoholic potash acts on acetylene di-iodide, $\text{CHI}:\text{CHI}$, acetylene being liberated; this change is analogous to the conversion of acetylene dibromide into acetylene and dibromovinyl ether. Di-iodacetylidene is very volatile, and has the odour of phenylic isocyanide, its vapour attacking the eyes; it is readily soluble in all organic solvents excepting petroleum. Slow oxidation in neutral solution converts it into carbonic oxide and tetriodethylene (compare Biltz, Abstr., 1897, i, 390), but the process is completely checked by the addition of caustic alkali.

Tri-iodovinyllic nitrate, $\text{CI}_2:\text{CI}\cdot\text{O}\cdot\text{NO}_2$, is obtained on dissolving di-iodacetylidene in cold, fuming nitric acid, which liberates carbonic anhydride and iodine; it crystallises from a mixture of benzene and petroleum in yellow needles, and melts at $109-110^\circ$.

When di-iodacetylidene is heated alone at $80-100^\circ$, it explodes violently, yielding iodine and carbon, but the solution in alcohol, glacial acetic acid, or petroleum, is not completely decomposed when heated with finely divided metals at 100° for 12 hours, although it gives rise to tetriodethylene. Acetylene is formed when di-iodacetylidene is reduced with sodium amalgam or sulphuric acid and zinc dust, and the hydrocarbon is also produced in small quantity along with carbonic oxide when the substance is treated with alcoholic sodium ethoxide at 100° ; excess of the latter agent gives rise to a mixture of ethylic iodacetate and *ethylic orthiodacetate*, $\text{CH}_2\text{I}\cdot\text{C}(\text{OEt})_3$, which is a colourless, pungent oil, and boils at 93° under a pressure of 14 mm.

Asymmetric dibromodi-iodethylene, $\text{CI}_2:\text{CBr}_2$, is prepared by adding bromine (1 mol.) dissolved in chloroform to a solution of di-iodacetylidene in the same medium; it crystallises from glacial acetic acid in yellowish leaflets, and melts at 95° . Alcoholic sodium ethoxide eliminates bromine from the compound, yielding di-iodacetylidene.

Bromacetylidene, $\text{CHBr}:\text{C}$, is identical with bromacetylene, prepared

by Sabanéeff from acetylene dibromide, by treating it with alcoholic soda. It boils at -2° , and burns spontaneously in air, yielding hydrogen bromide, carbon, carbon monoxide, and carbonic anhydride; in a very limited atmosphere, combustion is slow, and acetylene dibromide is produced. The vapour is poisonous, and has the odour of phosphorus vapour; moreover, its solutions in dilute nitric acid, water, or alcohol, which have the odour of ozone, exhibit phosphorescence during many days, and give ozone reactions. Although bromacetylidene acts vigorously with halogens and halogen hydrides, it is indifferent towards ethylic hypochlorite.

Bromacetylidene di-iodide (*di-iodacetylidene hydrobromide*, or *asymmetric di-iodobromethylene*), $\text{CHBr}\cdot\text{CI}_2$, is obtained by passing bromacetylidene into an ethereal solution of iodine; it boils at 104° under a pressure of 10 mm. Alcoholic sodium ethoxide, or potash, converts it into di-iodacetylidene, which is also produced under the influence of alcoholic sodium phenoxide and alcoholic potassium acetate (at 100°); in this respect, it resembles ethylic bromocyanacetate, from which hydrogen bromide is eliminated under similar conditions. Di-iodacetylidene hydrobromide, however, undergoes no change when heated with sodium acetate and a small quantity of glacial acetic acid at 150° during 12 hours, and it is also indifferent towards silver acetate at 100° .

Tri-iodobromethylene, $\text{CI}_2\cdot\text{CBrI}$, is a bye-product in the preparation of the foregoing substance, and remains as a crystalline residue in the distilling flask; it crystallises from glacial acetic acid in yellowish leaflets, and melts at 135° . Alcoholic sodium ethoxide, or potash, converts it into di-iodacetylidene, which is also produced under the influence of sunlight.

The paper concludes with a discussion of the general behaviour of trihaloid and tetrahaloid derivatives of methane, and of certain phases of molecular rearrangement, on the lines already laid down.

M. O. F.

Action of Sulphuric Acid on Coal Gas. By P. FRITZSCHE (*J. pr. Chem.*, 1897, **56**, 258—265).—Berthelot (this *Journal*, 1876, ii, 183) has shown that when coal gas is passed through concentrated sulphuric acid, brown coloured substances are formed consisting of condensation products of substituted acetylenes. The author now shows that the nature of the products varies with the coal gas examined and in no case is the formation of these substances so simple as Berthelot's experiment suggested.

Coal gas freed from benzene and hydrogen sulphide was treated with concentrated sulphuric acid in iron vessels under a pressure of about 4 atmospheres. From the oily product thus obtained crystals separated on cooling, which proved to be the iron salt of a sulphonic acid. By treating all the oil with caustic soda, considerable amounts of the sodium salt of the same acid were obtained, and from this the *copper*, *sodium*, *ammonium*, *iron*, and *calcium* salts were prepared.

The *free acid*, liberated from the copper salt by treatment with hydrogen sulphide, forms white crystals readily soluble in water, is very stable, not being acted on by hot concentrated sulphuric acid,

and appears to be the sulphonic acid of a substance having the formula $C_{15}H_{26}O$. This may probably be cedar camphor, a supposition supported by the fact that camphors, as a rule, form stable sulphonic acids.

At least one other substance of similar constitution exists in the mother liquor from the sodium salt, and will be further investigated.

A. W. C.

Preparation of Bromonitromethane. By JOSEPH TCHERNIAC (*Ber.*, 1897, 30, 2588).—Bromonitromethane can readily be prepared by dissolving 15 grams of nitromethane in baryta water, cooling with ice and adding the solution to 39 grams of bromine covered with pieces of ice; the excess of bromine is then removed by sulphurous acid and the liquid distilled, when 18 grams of the pure compound is obtained.

A. H.

Acetylene Di-iodide. By GUILLAUME L. J. DE CHALMOT (*Amer. Chem. J.*, 1897, 19, 877—878).—In reference to the preparation of this substance by Biltz (*Abstr.*, 1897, i, 389), the author states that he obtained it some years ago in preparing ethylene tetriodide by Maquenne's method, using calcium carbide instead of barium carbide. The alcoholic washings of the crude tetriodide were diluted with water, when acetylene di-iodide was precipitated together with some oily matter. It crystallised from alcohol or ether in long, transparent needles and melted at 82° . By adding iodine to a solution of acetylene in potassium hydroxide solution, no ethylene tetriodide was formed, but a white precipitate was produced which crystallised from benzene in needles; it has a very pungent odour and attacks the mucous membrane especially of the eyes. A similar compound prepared with bromine is an oil which takes fire spontaneously on exposure to the air and has a very disagreeable odour.

E. W. W.

Regularities in the Boiling-points of Isomeric Aliphatic Compounds. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1897, 30, 2784—2791).—When the boiling points of the various amylic and hexylic alcohols are compared amongst each other, the same regularities are observed as with the constant of velocity of reaction (this vol., i, 119), the normal compounds having the higher boiling point, which is lowered by the introduction of side chains, according to their position, size, and number, in the manner already described. The alcohols are peculiarly favourable for such a comparison, because the greatest difference of boiling point exhibited by a set of isomerides is larger than in the case of other compounds, and, moreover, increases with the number of carbon atoms present. But similar regularities can be observed with other compounds of the type $X \cdot [CH_2]_n \cdot CH_3$ and their isomerides, where $X = I, CH_3 \cdot COO, NH_2,$ or $COOH$; and also with compounds of the type $X \cdot [CH_2]_n \cdot X$ and their isomerides, where $X = Br, OH,$ or CH_3 .

C. F. B.

2:4-Hexadi-inediol-1:6. By ROBERT LESPIEAU (*Compt. rend.*, 1896, 123, 1295—1296).— $OH \cdot CH_2 \cdot C \equiv C \cdot C \equiv C \cdot CH_2 \cdot OH$, is obtained when the copper derivative of propargylic alcohol is oxidised with potassium ferrieyanide and the product treated with ether. It is a colourless, crystalline solid melting at $111-112^{\circ}$ and turning

yellow or rose-coloured under the action of heat or light. It dissolves in water, alcohol, ether, and acetic acid. The most suitable agent for purification is boiling benzene, from which it crystallises on cooling. At -15° , it combines with 4 atoms of bromine. Its glycolic nature was proved by converting it into the diacetin. The *dimethyl ether*, $\text{OMe}\cdot\text{CH}_2\cdot\text{C}:\text{C}:\text{C}:\text{C}:\text{CH}_2\cdot\text{OMe}$, is obtained when methyl propargyl ether is oxidised. It is a colourless liquid which turns brownish-red on exposure to light; it melts at -9° , distils at $104.5\text{--}105.5^{\circ}$ under a pressure of 12—13 mm., has the sp. gr. = 0.9969, and at -15° combines with 4 atoms of bromine. J. J. S.

New Synthesis of Glycerol and of Dihydroxyacetone. By OSCAR PILOTY (*Ber.*, 1897, 30, 3161—3169. Compare *Abstr.*, 1897, i, 453).—When bromine acts on an aqueous solution of dihydroxyacetoxime (*loc. cit.*), nitrous oxide is eliminated, and dihydroxyacetone produced; reduction of the ketone with sodium amalgam converts it into glycerol, a step which completes the synthesis of that substance from formaldehyde. The different stages by which the synthesis is effected are the following. Nitromethane converts formaldehyde into tertiary nitrotrihydroxybutane, $\text{NO}_2\cdot\text{C}(\text{CH}_2\cdot\text{OH})_3$, which on reduction yields hydroxylaminotrihydroxybutane, $\text{OH}\cdot\text{NH}\cdot\text{C}(\text{CH}_2\cdot\text{OH})_3$; oxidation with mercuric oxide eliminates formaldehyde from this substance, giving rise to dihydroxyacetoxime, $\text{OH}\cdot\text{N}:\text{C}(\text{CH}_2\cdot\text{OH})_2$, which is then treated in the manner already indicated.

Dihydroxyacetone, $\text{CO}(\text{CH}_2\cdot\text{OH})_2$, is prepared by adding bromine (15 grams) to a solution of dihydroxyacetoxime (10 grams) in water (100 c.c.), the temperature being allowed to rise to 40° ; by a method of purification which is detailed in the original paper, the ketose is obtained as a white solid, which crystallises from much boiling acetone in flat, prismatic plates melting at $68\text{--}75^{\circ}$. Dihydroxyacetone dissolves with extraordinary readiness in water, and tastes sweet, producing a cooling sensation on the tongue; it exerts vigorous reducing action on cold Fehling's solution, and when a 1 per cent. solution is boiled with the agent, the reduction effected is equal to that produced by an equal weight of grape sugar under the same conditions. The ketose, however, is not fermented by yeast. When the aqueous solution is treated with phenylhydrazine and acetic acid, the phenylosazone is produced, crystallising from benzene in elongated, prismatic leaflets melting at 132° ; this compound was obtained by E. Fischer and Tafel (*Abstr.*, 1888, 1264) from glycerose, and by Piloty and Ruff (*Abstr.*, 1897, i, 454) from dihydroxyacetoxime. The *sodium hydrogen sulphite* compound crystallises from dilute alcohol in stellate groups of slender needles. Dihydroxyacetone is reduced to glycerol by means of sodium amalgam in an aqueous solution of aluminium sulphate.

If the syrup from which dihydroxyacetone is first separated remains for some time without being sown with a crystal of the substance, a *compound* separates in minute crystals, and when recrystallised from alcohol, melts at 155° ; it has a sweet taste, reduces hot Fehling's solution, and appears to be identical with the substance obtained from dihydroxyacetone when an attempt is made to crystallise it from alcohol. Another *compound* is produced when the solution of di-

hydroxyacetone is evaporated in a vacuum at 65—70°; it is a white solid, resembling crude starch, and is insoluble in absolute alcohol. It dissolves very slowly in boiling water, and yields, with dilute acids, a turbid liquid which reduces cold, alkaline copper oxide. These two substances are doubtless polymerides or anhydrides of dihydroxyacetone.

The author discusses the part which is played by formaldehyde in the chemistry of vegetable physiology.

M. O. F.

Reactions of Potassium Ferricyanide with Glucose and their Application to Volumetric Analysis. By N. TARUGI and G. NICHIOTTI (*Gazzetta*, 1897, 27, ii, 131—153).—The authors show that the reaction between potassium ferricyanide and glucose in boiling potash solution depends on the concentration; the reaction is represented in normal solutions by the equation $10K_3FeCy_6 + 17KHO + 2C_6H_{12}O_6 = 10K_4FeCy_6 + 2K_2CO_3 + 2C_2H_3O_2K + 12H_2O + C_6H_{11}O_7K$, in N/10 solutions by the equation $10K_3FeCy_6 + 21KHO + 4C_6H_{12}O_6 = 10K_4FeCy_6 + C_6H_{11}O_7K + 8C_2H_3O_2K + 2KHCO_3 + 46H_2O$, and in N/40 solutions by the equation $10K_3FeCy_6 + 19KHO + 5C_6H_{12}O_6 = 10K_4FeCy_6 + 5C_6H_{11}O_7K + 4KHO + 10H_2O$. The course of these reactions was followed by determinations of the velocity of reaction.

Working with solutions of either of these three concentrations, with potash, glucose, and potassium ferricyanide, if the concentrations of two of the solutions are known, that of the third can be determined.

W. J. P.

Caroubinose and *d*-Mannose. By W. ALBERDA VAN EKENSTEIN (*Compt. rend.*, 1897, 125, 719).—The caroubinose described by Effront (*Compt. rend.*, 1897, 125, 309) is identical with the *d*-mannose described by the author (*Abstr.*, 1896, i, 272). The higher rotatory power observed by Effront is probably due to the presence of products of incomplete saccharification, possibly a bihexose derived from two mannose groups.

C. H. B.

Biological Production of Levulose from Mannitol. By CAMILLE VINCENT and BÉNÉDICT DELACHANAL (*Compt. rend.*, 1897, 125, 716—717).—When the ferment of sorbose is cultivated in a mineralised peptone solution containing 3 per cent. of mannitol, the mannitol is oxidised and converted into levulose. This change is the converse of the production of mannitol from levulose by the action of sodium amalgam.

C. H. B.

Humin Formation from Sugar on Oxidation with Potassium Permanganate. By H. VON FEILITZEN and BERNHARD TOLLENS (*Ber.*, 1897, 30, 2581—2584).—The authors do not agree with Benni's conclusions, and find that the brown precipitate formed by the oxidation of sugar with potassium permanganate has nothing to do with humin substance, but consists for the most part of oxide of manganese and potassium hydroxide, and contains only 0.5—0.7 per cent. of carbon.

J. F. T.

Hydrolysis of Starch by Diastase. By PAUL PETIT (*Compt. rend.*, 1897, 125, 355—357).—Starch was hydrolysed at 70° with precipitated diastase (1 per cent.) until the colour with iodine no longer changed.

The red coloration thus obtained could only be destroyed by the addition of larger quantities of diastase.

The liquid which gave the red coloration was concentrated, and after cooling, fermented with yeast; after filtration and concentration a syrup was obtained, which was precipitated with alcohol, purified, washed and dried thoroughly. The last traces of sugar were removed by extracting with absolute alcohol in a Soxhlet tube for 8 hours. Dextrin D as thus obtained is a white, non-hygroscopic powder; its composition is probably $(C_6H_{10}O_5)_3$, its specific rotatory power $\alpha_D = +176.4^\circ$, and its reducing power $R = 14.93$. It gives no osazone, and yields glucose when hydrolysed by boiling for about 3 hours with dilute hydrochloric acid; when boiled for a shorter time, a mixture of glucose with a biose is obtained, the osazone of the latter melting at $180-181^\circ$. The action of diastase on dextrin D has also been studied.

J. J. S.

Aliphatic Carbon Chains. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1897, 30, 2775—2784).—This paper gives the results of an investigation, the details of which have been published in *J. Russ. phys.-chem. Soc.*, 29, 444. The velocity of reaction of primary amines with allylic bromide in fifteen times their weight of benzene and at 100° has been examined; the values of the constant of velocity $k = (A - \frac{1}{2}x)/(A - x)t$ are tabulated below. As regards nomenclature, the Greek letter indicates the position of the side chain (which, with but one exception, is methyl); thus $NH_2 \cdot CHMe \cdot CHMe \cdot CH_3$ is $\alpha\beta$ -amylamine.

	Methyl-amine.	Ethyl-amine.	Propyl-amines.	Butyl-amines.	Amyl-amines.	Hexyl-amine.
Normal	8302	3807	3783	3886	3790	3537
γ					2985	
β				2759		
α			1257	1240	1189	
[α -ethyl]					[672]	
$\alpha\beta$					586	
$\alpha\alpha$				314	270	

Inspection of the table shows that the formation of a carbon chain by the change from methylamine to ethylamine is attended by a marked diminution of the constant. Once a chain is formed, however, the elongation of this chain, so long as it remains primary, has but little effect on the constant, the normal primary aliphatic amines, with the exception of methylamine, having approximately the same constant. The introduction of a side chain lowers the constant, and the more so the nearer it is to the amido-group; in the one case of α -ethyl, as compared with α -methyl (amylamine), it is seen that the elongation of a side chain produces a further diminution of the velocity of reaction. The introduction of a second side chain further diminishes the velocity, and in the same manner as before, a minimum value of the constant being obtained when both side chains are in the α -position.

The old measurements of the rate of etherification of aliphatic alcohols show the same regularities, the hydroxyl group here replacing the amido-group of the amines. C. F. B.

Action of Hydrogen Sulphide and of Carbon Bisulphide on Trimethyltrimethylenetriamine. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1896, [vii], 9, 119—133).—This work has been published previously in an abridged form (see Abstr., 1897, i, 456). J. J. S.

Derivatives of Prozan. By JOHANNES THIELE and WILHELM OSBORNE (*Ber.*, 1897, 30, 2867—2869).—By the action of potassium cyanide on diazoguanidine nitrate, there is obtained, beside much amidotetrazole, *diazoguanidine cyanide*, $\text{N:C:N:N:NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$; this is a yellowish substance which decomposes above 200° ; in it the CN group can be converted into $\text{CO}\cdot\text{NH}_2$, $\text{C}(\text{NH}_2)\cdot\text{NH}$, $\text{C}(\text{NH}_2)\cdot\text{NOH}$, COOEt , &c., by the usual methods. These are the first aliphatic diazo-amido-compounds that have been obtained.

Formamidodiazocamidoprozan, $\text{NH}_2\cdot\text{CO}\cdot\text{N:N:NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$, crystallises with $1\text{H}_2\text{O}$ in yellow needles which explode at 140° ; the colourless *hydrochloride* explodes at 141° . *Ethylic formamidodiazocamidoprozan*, $\text{COOEt}\cdot\text{N:N:NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$, is yellow, and melts at 162° . Both of these substances unite with sulphurous acid in the cold, and the products, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{SO}_3\text{H})\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$ and $\text{COOEt}\cdot\text{NH}\cdot\text{N}(\text{SO}_3\text{H})\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$, must be regarded as derivatives of prozan, $\text{NH}_2\cdot\text{NH}\cdot\text{NH}_2$. It was not possible, however, to isolate prozan from them; unlike hydrazine, it seems to be very unstable. C. F. B.

Action of Sodium on Methyl Propyl Ketone and on Acetophenone. By PAUL C. FREER and ARTHUR LACHMANN (*Amer. Chem. J.*, 1897, 19, 878—890).—The action of sodium on a dilute solution of methyl propyl ketone in ether gives rise to a white, flocculent precipitate of the formula $\text{C}_5\text{H}_9\text{ONa}$, hydrogen being evolved; this substance is fairly stable in dry air, but is decomposed by water. As it is probably of a complex nature, like the analogous sodium acetone, the action of sodium suspended in ether on a mixture of the ketone with benzoic chloride was investigated; the product was treated with alkali, which dissolved a large quantity of benzoic acid, and a trace of an undetermined fatty acid.

Dibenzoylmethyl Propyl Ketone, $\text{CHBz}_2\cdot\text{COPr}$ or $\text{OH}\cdot\text{CPh}\cdot\text{CBz}\cdot\text{COPr}$.—This melts at 115° , is almost insoluble in cold alcohol and ether, and is best purified by dissolving it in boiling alcohol, from which it separates in white, amorphous flakes. It gives an intense red coloration with ferric chloride, is soluble in alkalis and alkali carbonates, and is slowly precipitated from such solutions by carbonic anhydride. By varying the strength of the alcohol from which it is crystallised, and the rate of cooling, the melting point of the product varies between 101° and 115° ; in some cases, also, it gives only a very faint ferric chloride reaction. This may be due to the existence of two modifications analogous to that of Claisen's similarly constituted dibenzoylacetylmethane (*Annalen*, 291, 73). It is only very slowly hydrolysed by alkalis. It gives several products with phenylhydrazine, one of which forms long needles, and melts at 110° .

The original ethereal solution contains the benzoyl compounds of methyl propyl ketone and of methyl propyl carbinol, and the *iso*-ketone $\text{CH}_3\cdot\text{CPr}\cdot\text{OH}$, seemingly in the form of its hydrogen chloride compounds. The action of benzoic chloride on sodium methyl propyl ketone would thus appear to be similar to its action on sodium acetone, and the sodium compound would have the constitution represented by the formula $\text{ONa}\cdot\text{CPr}^a\cdot\text{CH}_3$.

By the action of sodium on a mixture of benzoic chloride and acetophenone under conditions similar to those described in the previous reaction, the authors obtained di- and tri-benzoylmethane from the alkaline extract, whilst the ethereal solution, on fractionation under 14 mm. pressure, yields an oil containing acetophenone and chlorinated derivatives. The thick tarry residue, on saponification with potash, gives benzoic acid and tribenzolymethane, and with dilute sulphuric acid at 160° , benzoic acid, acetophenone-pinacone, and a ketone which boils at 180 – 182° under 14 mm. pressure. This ketone contains chlorine, gives a deep red coloration with ferric chloride, is insoluble in alkalis, and reacts with phenylhydrazine. The reaction is, therefore, similar to that with methyl propyl ketone, except that no *iso*-ketone benzoate is formed. Hence sodium acetophenone has a constitution represented by the formula $\text{ONa}\cdot\text{CPh}\cdot\text{CH}_3$.

The action of sodium on mesityl oxide was also investigated, but no definite results were obtained.

Diethyl ketone in ethereal solution is attacked by sodium with liberation of hydrogen, forming a white sodium compound, which seems to be more stable than sodium acetone or sodium methyl propyl ketone, but resembles them in properties.

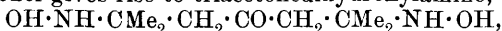
E. W. W.

Action of Hydroxylamine on Phorone. By CARL D. HARRIES and FRITZ LEHMANN (*Ber.*, 1897, 30, 2726–2737. Compare Abstr., 1897, i, 211).—It has been several times observed that unsaturated ketones differ considerably from saturated ones in their behaviour towards hydroxylamine. The authors, for instance, have shown that phorone gives rise to three substances, none of which is the normal oxime (*loc. cit.*), and three hydroxylamine derivatives have been also obtained from benzylideneacetophenone (Claus, Abstr., 1897, i, 189); Tiemann has found that isocamphorone yields hydroxylaminodihydrocamphorone-oxime under the influence of alcoholic hydroxylamine when the ketone is in excess (*loc. cit.*, i, 200), and Knoevenagel, generalising from the behaviour of ketones of the type $\text{RCO}\cdot\text{CR}\cdot\text{CHR}$, has shown that they are converted into derivatives of the constitution

$$\begin{array}{c} \text{CHR}\cdot\text{CHR} \\ \text{CR} = \text{N} > \text{O} \end{array}$$

(compare Abstr., 1896, i, 189).

Returning to their study of the action of hydroxylamine on phorone, the authors find that treatment with a cold solution of the base in absolute alcohol gives rise to triacetonedihydroxylamine,



the anhydride, $\text{CO} < \begin{array}{c} \text{CH}_2\cdot\text{CMe}_2\cdot\text{NH} \\ \text{CH}_2\cdot\text{CMe}_2\cdot\text{NH} \end{array} > \text{O}$, being formed if the liquid is warmed with water and free alkali; triacetonehydroxylamine, $\text{CO} < \begin{array}{c} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}_2\cdot\text{CMe}_2 \end{array} > \text{NOH}$, described in the previous paper (Abstr., 1897,

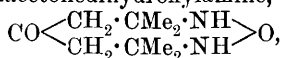
i, 212), is produced by the action of hydroxylamine (1 mol.) on phorone in presence only of free sodium ethoxide ; this is analogous to the conversion of phorone into triacetoneamine, $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{smallmatrix} \text{NH}$, under the influence of ammonia.

Triacetonedihydroxylamine,



is obtained by adding a solution of free hydroxylamine (2 mols.) in 400 c.c. of methylic alcohol to 50 grams of phorone dissolved in 100 c.c. of the same medium ; after 4 days, the liquid is diluted with ether (2 vols.), filtered, and treated with anhydrous oxalic acid (33 grams) dissolved in ether, the oxalate which is thus obtained being finally dissolved in dilute hydrochloric acid and mixed with potassium carbonate. The base is a colourless, syrupy liquid, which boils at 135° under a pressure of 20 mm., without undergoing decomposition if small quantities are manipulated ; it dissolves readily in water, and is very soluble in alcohol, ether, light petroleum, and benzene. It has a vigorous reducing action on cold Fehling's solution, and is feebly alkaline towards turmeric ; prolonged treatment with boiling water is without influence on the substance. The *hydrochloride* crystallises from a mixture of absolute alcohol and ether in hygroscopic leaflets ; it begins to melt at 116° , and effervesces at 130° . When the aqueous solution is boiled in a reflux apparatus, the hydrochloride of triacetone-dihydroxylamine anhydride is produced. The *oxalate*, prepared in the manner described, crystallises from dilute alcohol in small prisms ; it melts and effervesces at 165° . The *dinitroso*-derivative, obtained by adding sodium nitrite to an aqueous solution of the hydrochloride, crystallises in leaflets, and is decomposed by concentrated caustic soda, which liberates gas. The compound is acidic in character, and does not reduce Fehling's solution ; it fails to give Liebermann's reaction.

The *anhydride* of triacetonedihydroxylamine,



has been already described (*loc. cit.*), and is prepared by heating phorone with free hydroxylamine (2 mols.) and a few c.c. of concentrated caustic soda, in a reflux apparatus, until the liquid has no action on Fehling's solution ; the *hydrobromide* and *hydriodide* crystallise in stellar aggregates of leaflets, the *oxalate* forms long needles, the *aurichloride* leaflets, and the *platinochloride* prisms.

When the dihydroxylamine derivative or its anhydride is reduced with zinc dust and hydrochloric acid, triacetonediamine is produced, identical with the compound obtained by Heintz from acetone and ammonia ; the base boils at 95° under a pressure of 12 mm., and the aqueous solution, when boiled alone or with hydrochloric acid, yields triacetoneamine. The *zinc* double salt crystallises from water in large plates containing water of crystallisation which is lost at 110° ; it decomposes at 208° . The *dioxalate* crystallises in small white needles, and melts and effervesces at 189° .

If the reduction of the dihydroxylamine derivative and its anhydride is carried out with sodium amalgam and dilute sulphuric acid, *triacetonealkdiamine*, $\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2$, is pro-

duced; this crystallises from ether in rhombic prisms, melts at 98—99°, and boils at 205—210°.

Triacetonehydroxylamine, $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{smallmatrix} \text{N} \cdot \text{OH}$, is prepared by allowing phorone, dissolved in methylic alcohol, to remain with free hydroxylamine (1 mol.) and free sodium methoxide (1 mol.) for several days, until the reducing action of the liquid on Fehling's solution is but slight (compare *loc. cit.*); the *hydriodide* crystallises from a mixture of alcohol and ether in yellowish prisms, becomes brown at 170°, and melts at 180°. The *oxalate* also forms prisms, and melts at 85°. The *benzoyl* derivative crystallises from light petroleum in needles, and melts at 117°. Reduction with sodium amalgam in acid solution converts triacetonehydroxylamine into the *base*, $\text{C}_9\text{H}_{21}\text{NO}_2$, which crystallises in leaflets, melts at 56—57°, and boils at 225—235°; the *aurochloride* crystallises in lustrous, golden prisms. Triacetonehydroxylamine induces temporary paralysis of the spinal nerves.

Experiments on the behaviour of mesitylic oxide towards hydroxylamine have led to the production of three monhydroxylamine derivatives.
M. O. F.

Ketonic Acetates. By A. COLLET (*Compt. rend.*, 1897, 125, 354—355. Compare Hunnius, *Abstr.*, 1878, p. 147).—An alcoholic solution of the brominated ketone is warmed with a slight excess of pure dry potassium acetate, and after removal of the potassium bromide the alcohol is distilled off on the water bath and the residue poured into cold water. The oily product is then separated, dried, and distilled under diminished pressure.

α-Benzoylethyllic acetate, $\text{CH}_3 \cdot \text{COO} \cdot \text{CHMeBz}$, obtained from bromopropionyl benzene, is a yellow oil with an aromatic odour; it is insoluble in water, but dissolves in alcohol or ether; its sp. gr. = 1.11, and it distils at 158—160° under a pressure of 20 mm. *α-Benzoylpropyllic acetate*, $\text{CH}_3 \cdot \text{COO} \cdot \text{CHEtBz}$, boils at 164—170° under a pressure of 25—30 mm. *α-Benzoylisopropyllic acetate*, $\text{CH}_3 \cdot \text{COO} \cdot \text{CHMe}_2\text{Bz}$, boils at 135—140° (at 15—20 mm.).

When hydrolysed with dilute soda or with baryta water, these acetates yield yellow liquids having the characteristic properties of acetols.
J. J. S.

Thio-organic Compounds of Arsenic. By N. TARUGI (*Gazzetta*, 1897, 27, ii, 153—166).—At a low temperature and in presence of sufficient sodium carbonate to neutralise the hydrochloric acid produced, arsenic trichloride acts on thioacetic acid in accordance with the equation $2\text{MeCOS} \cdot \text{H} + \text{AsCl}_3 = (\text{MeCOS})_2\text{AsCl} + 2\text{HCl}$. The compound of the composition $(\text{MeCOS})_2\text{AsCl}$ is a yellowish liquid, of sp. gr. = 1.102, which begins to deposit arsenic trisulphide at 5°, and decomposes at lower temperatures on exposure to light; it is more stable when dissolved in alcohol, ether, chloroform, or carbon bisulphide.

On prolonged boiling, thioacetic acid and arsenic tri-iodide interact with formation of *arsenic sulphiodide*, AsSI , a crystalline, yellow powder insoluble in the ordinary solvents; it is decomposed by alkali hydroxides in accordance with the equation $3\text{AsSI} + 12\text{NaHO} = \text{Na}_3\text{AsS}_3 + 2\text{Na}_3\text{AsO}_3 + 3\text{NaI} + 6\text{H}_2\text{O}$, and is identical with the product

obtained by heating arsenic sulphide with iodine or arsenic trioxide. The reaction by which arsenic sulphiodide is produced, namely, $\text{AsI}_3 + \text{MeCOSH} + \text{H}_2\text{O} = \text{AsSI} + \text{MeCOOH} + 2\text{HI}$, is a reversible one.

At low temperatures, thioacetic acid reacts with arsenites in accordance with the equation $2\text{MeCOSH} + \text{Na}_3\text{AsO}_3 = (\text{MeCO})_2\text{S} + \text{NaAsOS} + 2\text{NaHO}$; at ordinary temperatures, arsenic trisulphide is precipitated.

In presence of iodine and at a low temperature, thioacetic acid and arsenites react with formation of a heavy oil of the composition $(\text{MeCOS})_2\text{As}_2\text{S}_3$; this is insoluble in water or organic solvents, slowly solidifies to a yellow mass, and when boiled with water yields acetic acid and arsenic trisulphide. This additive compound is also obtained by the action of acetic sulphide on arsenic trisulphide at ordinary temperatures. When the liquid substance is treated with gaseous ammonia, a compound of the composition $[\text{MeCOS} \cdot \text{As}(\text{NH}_2)]_2\text{S}_2$ is obtained as a yellow powder which is sparingly soluble in cold organic solvents, but dissolves in mineral acids with immediate precipitation of arsenic trisulphide; it is converted into a substance of the composition $[\text{MeCOS} \cdot \text{As}(\text{OH})]_2\text{S}_2$ by suspending it in cool dilute acetic acid and adding potassium nitrite. On treating the additive compound with an alcoholic solution of aniline, a substance of the composition $[\text{MeCOS} \cdot \text{As}(\text{NHPh})]_2\text{S}_2$ is obtained as a yellowish powder; a similar compound is obtained with paratoluidine. Both give the above dihydroxy-compound when treated with nitrous acid, and the toluidine derivative yields dehydrothiotoluidine when treated with dilute hydrochloric acid.

W. J. P.

γ -Ketonic Acids. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1897, 27, ii, 176—182).—On treating β -methyllevulinic acid with methylic iodide and sodium ethoxide, the author did not obtain $\beta\beta$ -dimethyllevulinic acid as was hoped, but a mixture of $\alpha\beta$ -dimethylglutaric acid and methylsuccinic acid. On treating ethylic levulinate or α - or β -methyllevulinate with methylic iodide and sodium ethoxide, a mixture is ultimately obtained which can be separated into two substances boiling at 100—110° and 200—210°; the fraction boiling at 100—110° gives semicarbazones identical with those of the original materials in the case of the α - and β -methyllevulinates, but not in the case of ethylic levulinate. The semicarbazone, $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_3$, of ethylic levulinate melts at 150°, whilst that from the ethylic levulinate recovered from the methylation melts at 141°; similarly, the respective hydrazones melt at 108° and 95—96°. The levulinic acid used was prepared from levulose and the discordant melting points are perhaps explained by Berthelot's observation (*Compt. rend.*, 1897, 123, 341) that such levulinic acid is a mixture of two acids.

W. J. P.

Dibasic Acids. By L. ÉTAIX (*Ann. Chim. Phys.*, 1896, [vii], 19, 356—407).—The author finds the best method of obtaining adipic acid to be Crum Brown and Walker's electrolytic method. Adipic chloride, $\text{C}_4\text{H}_8(\text{COCl})_2$, after several fractionations under reduced pressure, forms a colourless liquid distilling at 125—128° under a pressure of 11 mm., but undergoing slight decomposition at the same time. Adipic

anhydride, $C_4H_8 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$, is obtained by the action of the chloride, diluted with a few cubic centimetres of anhydrous ether, on sodium adipate; it crystallises from benzene in small, mammillated masses melting at $95-100^\circ$; a small quantity of the same compound is obtained when adipic acid is boiled with acetic chloride for several hours. Adipic chloride reacts with benzene in the presence of aluminium chloride, yielding 1:6-*diphenylhexanedione*-1:6, $COPh \cdot [CH_2]_4 \cdot COPh$, which crystallises from alcohol in yellowish needles melting at $102-103^\circ$; the corresponding *dioxime* melts at $216-218^\circ$. Ammonia reacts with a benzene solution of adipic anhydride, yielding adipamide and *adipamic acid*, the latter of which crystallises in microscopic needles melting at $125-130^\circ$.

The author has attempted to prepare diacetylpmelic acid, $CH_2(CHAc \cdot CH_2 \cdot COOH)_2$, by the condensation of formaldehyde with acetopropionic acid in the presence of diethylamine, but without success.

Concise details are given for the separation of suberic and azelaic acids. *Suberic chloride*, $COCl \cdot [CH_2]_6 \cdot COCl$, decomposes to a small extent when distilled under diminished pressure; it is an oil boiling at $162-163^\circ$ under 15 mm. pressure; the anhydride (compare Anderlini, Abstr., 1894, i, 499) is obtained by the action of the chloride on sodium suberate and crystallises in minute needles melting at $65-66^\circ$ (Anderlini, 52— 63°). *Dibenzoylhexane* (1:8-*diphenyloctanedione*-1:8) melts at $83-85^\circ$ and its *dioxime* at $192-193^\circ$. ω -*Benzoylheptoic acid*, $COPh \cdot [CH_2]_6 \cdot COOH$, is also obtained in the preparation of the dibenzoyl compound; it crystallises in brilliant plates melting at 78° , and is but sparingly soluble in water. *Suberamide* melts at 216° and *suberic acid*, obtained together with the amide by the action of dry ammonia on a benzene solution of the anhydride, crystallises in needles melting at $125-127^\circ$ (compare Arppe, *Zeit. f. Chem.*, 1865, 300).

Azelaic chloride, $C_7H_{14}(COCl)_2$, is a colourless liquid boiling at 165° under a pressure of 13 mm., but is partially decomposed at the same time. The anhydride melts at $56-57^\circ$ (Anderlini gives $52-53^\circ$). *Dibenzoylheptane*, $COPh \cdot [CH_2]_7 \cdot COPh$, separates from alcohol in colourless crystals melting at 44° , and yields a *dioxime* which could not be obtained in a pure state. *Azelamide*, $CONH_2 \cdot C_7H_{14} \cdot CONH_2$, melts at 172° , and *azelaic acid*, $CONH_2 \cdot C_7H_{14} \cdot COOH$, at $93-95^\circ$.

Sebamid acid, $CONH_2 \cdot [CH_2]_8 \cdot COOH$ melts at 170° , and *sebamid* at 208° . The author points out that substituted succinic acids readily yield anhydrides, that oxalic, malonic, and substituted malonic acids do not yield anhydrides under any conditions, and that glutaric acid, substituted glutaric acids, adipic, suberic, azelaic and sebacic acids yield anhydrides, but not very readily.

J. J. S.

Substituted Succinic Acids. By KARL AUWERS (*Annalen*, 1897, 298, 147—181. Compare Abstr., 1896, i, 639).—The author has continued the investigation of asymmetric and symmetric methyl-ethylsuccinic acids, and has established the identity of the former with isopimelic acid obtained from amylen bromide (compare *loc. cit.*).

Tertiary butylmalonic acid and the two stereoisomeric $\alpha\beta$ -dimethylglutaric acids are the only members of the group of 24 isomeric acids having the formula $C_7H_{12}O_4$ which have not been yet characterised. (Compare Montemartini, Abstr., 1896, i, 667).

I. [With R. FRITZWEILER].—The symmetrical methylethylsuccinic acids are prepared by the action of sodium on a mixture of ethylic methylmalonate and ethylic α -bromobutyrate, the details of the method, and the means by which the products are isolated, being described in the original paper. The fumaroid form crystallises from hot water in long, flat needles melting at 180° when heated with moderate rapidity, and at 177 – 179° when the temperature rises slowly; if rapidly heated, it melts at 182° , and water is eliminated at 190° . It dissolves readily in alcohol, ether, and acetone, and with difficulty in chloroform, being insoluble in petroleum; 3.05 parts dissolve in 100 parts of water at 17° . Metallic salts yield precipitates when added to a solution of the sodium salt, and calcium chloride gives rise to a crystalline salt when the liquid is boiled; the calcium salt obtained from the acid and calcium carbonate crystallises in colourless, anhydrous leaflets, being evidently different from the salt obtained by Bytschichin and Zelinsky, which contains $5H_2O$. The malenoid acid crystallises from water in stellate aggregates of slender, lustrous needles, melts at 101 – 102° , and loses water at 160° . It is readily soluble in organic solvents, excepting petroleum, which dissolves it with difficulty; 16.1 parts dissolve in 100 parts of water at 13° . Metallic salts give rise to precipitates, and calcium chloride produces a heavy precipitate in the cold solution, distinguishing this form from the fumaroid acid; the calcium salt contains $1H_2O$. The malenoid acid is obtained when the fumaroid modification is boiled for 3 hours, or heated at 210 – 220° during $8\frac{1}{2}$ hours; it is also produced in quantity amounting to 10 per cent. when the fumaroid acid is heated with 18 per cent. hydrochloric acid at 180 – 190° during 14 hours, the reverse action taking place with much greater readiness.

The *paratolilic acid* of the fumaroid acid crystallises from dilute alcohol in colourless, slender needles, and melts at 175 – 176° ; the *paratolil* also forms needles, and melts at 109 – 110° . Another *compound* is produced when an attempt is made to prepare the tolil at high temperatures; it crystallises from petroleum, and melts at 86 – 89° . The *anilic acid* and *anil* melt at 164 – 165° and 103 – 104° respectively.

The *paratolilic acid* of the malenoid form crystallises from dilute alcohol in lustrous leaflets, and melts at 147 – 148° ; the *paratolil* is identical with the derivative prepared from the fumaroid acid. The *anilic acid* and β -*naphthil* melt at 139 – 140° and 159 – 160° respectively; the *anil* is identical with the compound obtained from the fumaroid acid.

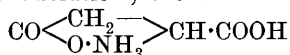
II. [With R. FRITZWEILER].—Asymmetric methylethylsuccinic acid crystallises from water in transparent, lustrous prisms belonging to the rhombic system, and melts at 103 – 104° ; in every particular, its properties agree with those ascribed to isopimelic acid, obtained by Bauer and Hell from amylene bromide. The *anilic acid* and *anil* melt at 168 – 169° and 60 – 61° respectively; the *paratolilic acid* and

paratolil melt at 162° and 64—65° respectively, whilst the β -*naphthilic acid* and β -*naphthil* melt at 179° and 96—97° respectively.

III. [With F. MAYER].—A specimen of amylene boiling at 29—35°, when converted into the bromide, then into the cyanide, and the latter hydrolysed, yielded a small proportion of isopropylsuccinic acid melting at 116°; the *paratolilic acid* crystallises from dilute alcohol, and melts at 143—144°.

IV. [With F. BETTERIDGE].—*Ethyl α -bromolaurinate* is a colourless oil which boils at 170—174° under a pressure of 11 mm. When heated with finely divided silver at 150° during 5½ hours, and the product hydrolysed, it yields *bidecylsuccinic acid*, the two isomerides being readily separable by petroleum. The *fumaroid* modification which dissolves but sparingly in petroleum, crystallises in white needles melting at 134°. The *malenoid* form is readily soluble, and separates in slender prisms melting at 74°. M. O. F.

Interconversion of Optical Antipodes. By PAUL WALDEN and O. LUTZ (*Ber.*, 1897, 30, 2795—2798).—*l*-Bromo- or *l*-chloro-succinic acid, which yields *l*-malic acid when treated with silver oxide, undergoes a gradual change of rotation when it is heated with 12 per cent. methyl alcoholic ammonia at 40—45°. When the dextrorotation has attained a maximum (after 10—12 hours), a substance can be isolated which melts at 122—124°, and has $[\alpha]_D = +27.6$ to $+29.2^\circ$ ($c = 20 - 1$) in aqueous, $= +40.8^\circ$ in 75 per cent. alcoholic solution; the composition $O \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH}_3 \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{COONH}_4$ is assigned to it. By treating this with the equivalent quantity of dilute hydrochloric acid, the free acid can be obtained; this melts at 148°, and has the rotation $[\alpha]_D = +9.7^\circ$ ($c = 3$) in aqueous solution; the constitution,

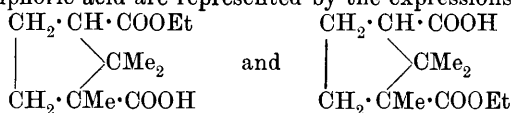


is assigned to it; with ammonia, it regenerates the original compound. By boiling it, or its ammonium salt, with barium hydroxide, the barium salt of *d*-malic acid is obtained. In a similar manner, *l*-malic acid can be obtained from *d*-bromo- or *d*-chloro-succinic acid C. F. B.

Law of Etherification of Unsymmetrical Aliphatic Dicarboxylic Acids. By RICHARD ANSCHÜTZ (*Ber.*, 1897, 30, 2652—2654. Compare following abstract).—Hydrogen α -ethyl mesaconate (*loc. cit.*), melting at 42°, obtained by the action of alcohol and hydrogen chloride on mesaconic acid, is readily hydrolysed by alkalis; the β -ethyl salt, however, which melts at 67—68°, yields the acid with difficulty when treated with hydrolytic agents. Its preparation from ethyl methylacetacetate, by the introduction of 2 atoms of bromine followed by treatment with barium carbonate and boiling water, indicates the constitution $\text{COOEt} \cdot \text{CMe} \cdot \text{CH} \cdot \text{COOH}$, the α -salt being represented by the formula $\text{COOH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{COOEt}$.

The author therefore concludes that when etherification of an unsymmetrical dicarboxylic acid is effected by means of alcohol and hydrogen chloride, the alkyl radicle is introduced more readily into that carboxylic group which is attached to a tertiary carbon atom than into one combined with quaternary carbon. According to this

generalisation, the hydrogen orthoethylic and hydrogen alloethylic salts of camphoric acid are represented by the expressions,



respectively, a conclusion at which Bredt has already arrived from other data.

The author prefers the terms α -salt and β -salt to ortho- and allo- respectively, the α -salt being the one which is most readily produced.

M. O. F.

Preparation of Ethereal Salts. By RICHARD ANSCHÜTZ and JULIEN DRUGMAN (*Ber.*, 1897, **30**, 2649—2652. Compare E. Fischer and Speier, *Abstr.*, 1896, i, 201).—The authors point out that the method of preparing ethereal salts described by Fischer and Speier (*loc. cit.*) can be advantageously modified by submitting the crude salt to direct distillation under considerably reduced pressure, excess of alcohol being previously removed by the same process.

Hydrogen α -methylic itaconate, $\text{CH}_2 \cdot \text{C}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOMe}$, crystallises from methylic alcohol and melts at 67° ; it boils at 149° under a pressure of 12 mm.

Hydrogen α -ethylic itaconate melts at 45° , and boils at 153° under a pressure of 12 mm.

Hydrogen ethylic fumarate melts at 66° , and boils at 147° under a pressure of 16 mm.

Hydrogen α -methylic mesaconate, $\text{COOH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{COOMe}$, melts at 36° , and boils at 145° under a pressure of 15 mm.; *hydrogen α -ethylic mesaconate* melts at 42° , and boils at 150° under a pressure of 15 mm. *Hydrogen β -methylic mesaconate*, $\text{COOMe} \cdot \text{CMe} \cdot \text{CH} \cdot \text{COOH}$, melts at 61 — 62° .

M. O. F.

δ -Methyluric Acid. By WOLF VON LOEBEN (*Annalen*, 1897, **298**, 181—187).—Three of the four theoretically possible methyluric acids have been already prepared, and in the case of two of these, the β - and γ -acids, the constitution has been recognised as that of 9-methyl-2 : 6 : 8-trioxypurine and 7-methyl-2 : 6 : 8-trioxypurine respectively (compare *Ber.*, 1897, **30**, 557). The α -methyluric acid, first obtained by Hill, is either 1-methyl-2 : 6 : 8-trioxypurine or 3-methyl-2 : 6 : 8-trioxypurine, whilst δ -methyluric acid is described in the present paper; the position of the methylic group in the latter acid, however, cannot be defined until the constitution of methylisodialuric acid, from which it is obtained by condensation with carbamide, has been determined.

Methylisodialuric acid, $\text{C}_5\text{H}_8\text{N}_2\text{O}_5$, prepared by oxidising methylisobarbituric acid with bromine water, is very readily soluble in water and separates in rosette-like aggregates. Barium hydroxide gives rise to a violet precipitate.

δ -Methyluric acid, $\text{C}_6\text{H}_6\text{N}_4\text{O}_3$, is obtained by heating methylisodialuric acid with carbamide and concentrated sulphuric acid at 100° and pouring the liquid into cold water; it separates from 500—600 parts of hot water in colourless, microscopic prisms containing $1\text{H}_2\text{O}$, which is removed at 150° . It gives the murexide reaction, and

oxidation with lead peroxide converts it into *methylallantoin*, $C_5H_8N_4O_3$ melting at 246° ; the methylallantoin obtained by Hill from α -methyluric acid melts at 225° . δ -Methyluric acid dissolves in 527 parts of boiling water, α -methyluric acid requiring 262 parts. M. O. F.

Oximes of Hexahydrobenzophenone and Hexahydropropionophenone. By W. SCHARVIN (*Ber.*, 1897, 30, 2862—2865. Compare Abstr., 1897, i, 612, where for 158° read 155° as the melting point of hexahydrobenzophenone α -oxime).—This α -oxime in ethereal solution reacts but slowly with phosphorus pentachloride, and the product is only slowly acted on by water; the final product was identified as benzoylhexamethyleneamine, $C_6H_{11}\cdot NH\cdot CPhO$ (von Baeyer, Abstr., 1894, i, 175). This is difficult to hydrolyse, but boiling with acetic anhydride converts it into acetylhexamethyleneamine. The β -oxime reacts much more readily with the pentachloride, and the product is readily converted by water into *hexahydrobenzanilide*, $C_6H_{11}\cdot CO\cdot NHPh$, together with some hexahydrobenzoic acid and aniline; this anilide is readily hydrolysed by strong sulphuric acid. In consequence of these reactions, the following configurations must be assigned to the two hexahydrobenzophenone oximes:



Hexahydropropionophenone, $C_6H_{11}\cdot COEt$, was obtained by the action of hexahydrobenzoic chloride (1 mol.) on zinc ethide (2 mols.); it boils at 195° , and does not form an additive compound with sodium hydrogen sulphite. Only one *oxime* could be obtained from it; this melts at $72\text{--}73^\circ$, and, in the Beckmann reaction, yields a product melting at 88° , which must be *propiono-hexamethyleneamide*, $C_6H_{11}\cdot NH\cdot COEt$, for it can be hydrolysed to propionic acid and hexamethyleneamine. The oxime must, therefore, have the configuration $C_6H_{11}\cdot C\cdot Et$.
OH·N

C. F. B.

The Benzene Nucleus. IX. By WILHELM VAUBEL (*J. pr. Chem.*, 1897, 56, 266—271).—The author shows that the change of eugenol into isoeugenol, and also the structure of diketochlorides and allied substances described by Zincke (Abstr., 1897, i, 507), may be satisfactorily explained by his benzene configuration. A. W. C.

Anethoil and its Isomerides. By WILLIAM R. ORNDORFF, G. L. TERRASSE, and D. A. MORTON (*Amer. Chem. J.*, 1897, 19, 845—870).—The authors, from a careful examination of anethoil and its isomerides, have arrived at the following conclusions.

(1) Eijkman's methylchavicol and Grimaux's estragole have the same molecular weight, and are metamerides of anethoil. The results of the investigation of these compounds by different chemists indicate their identity. (2) Liquid metanethoil also has the same molecular weight as anethoil; from its chemical behaviour, in which it closely resembles anethoil, and also from its physical properties, it is to be

regarded as a stereoisomeride of anethoil, and is probably the *trans*-compound, $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ | \\ \text{Me} \cdot \text{C} \cdot \text{H} \end{array}$ (p) (3) Anisoin, the resinous polymeric

modification of anethoil, acts as a colloid towards solvents such as ethylic acetate, acetone, and benzene. (4) Solid met-anethoil and the liquid isonethoil both have a molecular weight twice that of anethoil, and hence should be named solid dianethoil and liquid dianethoil respectively. As they both behave like saturated compounds, they are possibly derivatives of tetramethylene. (5) By heating anethoil under pressure at 250—275°, it is transformed into isonethoil, the methylic ether of paracresol and the methylic ether of parapropylphenol, the tendency under these conditions being apparently to form saturated compounds.

In determining the molecular weights of liquids such as anethoil by means of the boiling point method with the apparatus devised by Orndorff and Cameron (Abstr., 1895, ii, 480), the condenser tube was contracted a little below the point where the solvent condensed and ran back into the flask, so that when thin glass bulbs containing the liquid were dropped into the upper part of the condenser, they broke on reaching this point, or, if not, could be broken by means of a rod. This method is said to be more convenient and more accurate than that recommended by Beckmann.

The authors have also suggested names for anethoil and its isomerides more in accordance with the suggestions of the Geneva Conference and with the present state of knowledge. For example, liquid met-anethoil is named 1'-propenylphenol-4-methyl ether. E. W. W.

Action of Nitrogen Chloride on Aniline, Methylaniline, and Dimethylaniline. By W. HENTSCHEL (*Ber.*, 1897, 30, 2643—2649).

—When aniline is treated in molecular proportion with a solution of nitrogen chloride in benzene, a rise of temperature occurs, and trichloroaniline is produced; this compound is also formed when chlorine is passed into aniline hydrochloride suspended in benzene. Acetanilide is converted into parachloroacetanilide on agitation with a benzene solution of nitrogen chloride.

Trichloromethylaniline, $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{NHMe}$, is prepared by passing chlorine into benzene containing methylaniline hydrochloride in suspension, and is also formed when the base is treated with nitrogen chloride dissolved in benzene; it melts at 28.5°, and boils at 256°. The *hydrochloride* crystallises in prisms, and softens above 100°; the *platinochloride* forms large, pale-yellow crystals. Oxidation of trichloromethylaniline hydrochloride with a solution of chromic acid gives rise to trichloroaniline, the azo-compound being produced when excess of the oxidising agent is employed; the azoxy-derivative is formed if the process is applied to warm solutions.

The action of nitrogen chloride on dimethylaniline yields a compound, $\text{C}_{24}\text{H}_{11}\text{N}_2\text{Cl}_{19}$, which crystallises from light petroleum and melts at 117°; it is insoluble in water, but is somewhat readily soluble in common organic solvents. When the compound is heated alone, hydrogen chloride is eliminated in quantity amounting to 18 per cent. of the substance taken. M. O. F.

**Formation of Chains. XX. Chloranilines. XXI. Nitrani-
lines. XXII. Nitrotoluidines.** By CARL A. BISCHOFF (*Ber.*, 1897,
30, 2760—2764; 2764—2768; 2769—2775. Compare this vol., i, 73).—
The reacting substances, $C_6H_3R'R''NH_2$ (2 mols.) and $CHBr\cdot COOEt$
(1 mol.), were heated for 4 hours at 100° (sometimes at 125 — 130° ;
the numbers referring to this temperature are given in brackets in
the table below), and the percentage extent to which the condensa-
tion had taken place was estimated by weighing the hydrobromide,
 $C_6H_3R'R''NH_2\cdot HBr$, that had separated, after washing it with warm
ether. From the ethereal filtrate, unchanged amine could be re-
moved by passing in gaseous hydrogen chloride and filtering, and
from this second filtrate the product of the condensation was isolated
by fractional distillation or by crystallisation. When the extent of
the reaction was very small at the temperatures mentioned, special
experiments were made at higher temperatures for the sole purpose of
isolating some of the product. In the table below is given the per-
centage amount of condensation between the amines and ethereal
 α -bromo-salts there enumerated; the numbers for the methylanilines
(toluidines) are taken from a previous investigation, and are inserted
here for purposes of comparison.

Ethylic salt.	2-Chloraniline.	2-Methylaniline.	2-Nitraniline.	2-Nitro-4-methylaniline.	3-Chloraniline.	3-Methylaniline.	3-Nitraniline.	3-Nitro-4-methylaniline.	4-Chloraniline.	4-Methylaniline.	4-Nitraniline.	4-Nitro-2-methylaniline.
Bromopropionate	61	54	0 (14)	0 (7)	87	94	59 (87)	71 (88)	92	92	5(81)	0 (42)
Phenylacetate ...	49	43	42	17 (36)	71	47	77	84 (82)	72	43	63	45 (60)
Isobutyrate	9	19	0 (2)	(3)	21	62	9 (23)	(42)	23	38	0 (8)	(3)

The author draws attention to the effect of the different groups in the different positions, in promoting or hindering the condensation; it is impossible to quote his remarks in full, however, and the regularities are, moreover, apparent on inspection of the table given. Here, as often previously, substitution in the ortho-position is frequently found to hinder the condensation most, whilst in the meta-position it has the most favourable influence.

The following new ethylic salts are described:—*Chloranilido- α -propionates*, $C_6H_4Cl\cdot NH\cdot CHMe\cdot COOEt$: *ortho* boils at 280 — 285° , *meta* at 288 — 294° (melting at $40\cdot3^\circ$), *para* at 300 — 306° . *Chloranilido- α -phenylacetates*, $C_6H_4Cl\cdot NH\cdot CHPh\cdot COOEt$: *ortho* melts at 53 — 54° , *meta* at 88 — $88\cdot5^\circ$, *para* at $87\cdot8^\circ$.—*Nitraniido- α -propionates*, $NO_2\cdot C_6H_4\cdot NH\cdot CHMe\cdot COOEt$, yellow; *ortho* melts at $142\cdot5^\circ$, *meta* at 203° , *para* at 86 — 87° ; *paranitranilido- α -propionic acid* (with H_2O) is yellow, melts at 147° , and is hygroscopic when anhydrous.

Nitranylido- α -phenylacetates, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CHPh} \cdot \text{COOEt}$, yellow; *ortho* melts at $69-69.5^\circ$, *meta* at $83-84^\circ$, *para* at $120-120.5^\circ$. *Paranitranylido- β -isobutyrate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{COOEt}$, is yellow, and melts at 74° .—*Nitrotoluidido- α -propionates*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{COOEt}$, $[\text{NO}_2 : \text{Me} : \text{NH} = 3 : 1 : 4]$ yellow, melts at 62° ; $[2 : 1 : 4]$ at 64° ; $[5 : 1 : 2]$ at $103-104^\circ$. *Nitrotoluidido- α -phenylacetates*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CHPh} \cdot \text{COOEt}$; $[3 : 1 : 4]$, yellowish-red, melts at 106° ; $[5 : 1 : 2]$, yellow, at 118.3° . *Nitrotoluidido-isobutyrate* $[2 : 1 : 4]$ is yellowish and melts at 80° .

C. F. B.

Conversion of Amines into Phenols. By JACOB MEYER (*Ber.*, 1897, 30, 2568—2569).—The observation that metaphenylenediamine evolved considerable quantities of ammonia and methylamine on methylation led to the general study of the behaviour of aromatic amines when treated with acids at high temperatures, and it was found that when the base was heated in a closed tube with either 1.15 per cent. hydrochloric acid, 20 per cent. sulphuric acid, solution of zinc chloride, &c., at $160-250^\circ$, a considerable quantity of the corresponding phenol was produced, the yield increasing with the temperature, although at high temperatures considerable quantities of resinous products were at the same time formed. Thus on heating 6 grams of metaphenylenediamine with 20 per cent. hydrochloric acid at 180° , 2 grams of resorcinol was produced, whilst from tetramethylmetaphenylenediamine 30 per cent. of resorcinol was obtained.

J. F. T.

Derivatives of Paramidodimethylaniline [*Dimethylparaphenylenediamine*]. By JOHANNES PINNOW and E. KOCH (*Ber.*, 1897, 30, 2860—2861).—When acetamidodimethylparaphenylenediamine is heated with methylic iodide in benzene solution for 10 hours at 100° , the acid radicle is not expelled, as in the case of the formamido-compound (*Abstr.*, 1894, 281), but the compound $\text{MeI} \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, melting at 226° , is formed. When this is treated with alcoholic lead acetate, the lead bromide first removed and then the rest of the lead by precipitation with hydrogen sulphide, and the filtrate finally evaporated down with hydrochloric acid, *trimethylparamidophenylum chloride hydrochloride*, $\text{MeCl} \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$, melting at 219° , is obtained; this has been used for the preparation of azo-dyes soluble in water.

C. F. B.

Combination of Metallic Acetates with Phenylhydrazine. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, 125, 611—612).—Zinc, cadmium, manganese, and cobalt acetates combine with phenylhydrazine to form compounds of the formula $\text{R} \cdot 2\text{N}_2\text{H}_3\text{Ph}$ where R represents one molecule of the metallic acetate. Nickel acetate under similar conditions yields the compound $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{N}_2\text{H}_3\text{Ph}$. The compounds are obtained by boiling the powdered salt with an alcoholic solution of phenylhydrazine for about 15 minutes and then filtering. The zinc compound forms rhomboidal plates which melt at 135° ; the cadmium compound, elongated prisms melting at 121° ; the manganese compound, monoclinic prisms melting at 97° ; the cobalt compound crystallises in rose-coloured prisms which melt below

125°; and the nickel compound forms greenish-blue prisms which do not melt at 260°. All the salts decompose readily when heated. They dissolve in water, alcohol, or chloroform, but not in ether, and their solutions give the reactions of the metallic salt and phenylhydrazine.

C. H. B.

Combination of Phenylhydrazine with Metallic Salts. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, 125, 714—716. Compare Abstr., 1897, i, 561, 562).—In addition to the compounds containing one molecular proportion of metallic salt and two molecular proportions of phenylhydrazine, nickel chloride, nickel sulphate, and cobalt bromide form compounds with 5 mols. of phenylhydrazine, whilst cobalt chloride and cobalt sulphate form compounds with 4 mols. They are obtained by the action of a large excess of phenylhydrazine on the metallic salt, and are only slightly soluble in alcohol or water in the cold and practically insoluble in ether or chloroform. They give the reactions of phenylhydrazine and the metallic salt that they contain, and they lose phenylhydrazine at 100°. $\text{NiCl}_2 \cdot 5\text{N}_2\text{H}_3\text{Ph}$ forms long, blue, rhomboidal lamellæ, $\text{CoCl}_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ forms prismatic crystals, $\text{CoBr}_2 \cdot 5\text{N}_2\text{H}_3\text{Ph}$ forms rhombic prisms, $\text{CoSO}_4 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ short prisms, and $\text{NiSO}_4 \cdot 5\text{N}_2\text{H}_3\text{Ph}$ also crystallises in prisms.

Lithium chloride yields the compound $\text{LiCl} \cdot 2\text{N}_2\text{H}_3\text{Ph}$, which crystallises in deliquescent, rhomboidal lamellæ, and the halogen salts of the metals of the calcium group also yield compounds which will be described subsequently.

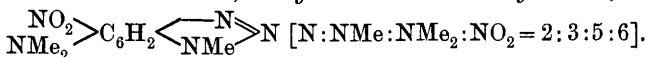
C. H. B.

Amidoazimidobenzene. By JOHANNES PINNOW and E. KOCH (*Ber.* 1897, 30, 2850—2860).—Methylaniline was converted into dinitromethylaniline by nitration with a mixture of dilute nitric and sulphuric acids; this was reduced with alcoholic ammonium sulphide to nitroamidomethylaniline, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{NHMe}$, and this, by treatment with sodium nitrite in dilute nitric acid solution, was converted into nitromethylazimidobenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N}(\text{NMe}) = \text{N}$ (Zincke and Helmert, Abstr., 1896, i, 300). By reducing this with tin and hydrochloric acid, *amidomethylazimidobenzene*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N}_3\text{Me}$, is obtained; this melts at 180°, the *hydrochloride* (with 2HCl), *hydrobromide*, *sulphate* (with $\frac{1}{2}\text{H}_2\text{SO}_4$) and yellow *picrate* (with $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$) at 249°, 237°, 292°, and 237° respectively, the mono-*acetyl* and -*benzoyl* derivatives at 237° and 228·5°. The *carbamide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{N}_3\text{Me}$ (from the hydrochloride and phenylic cyanate), *phenylcarbamide*,



and *phenylthiocarbamide* (from the base and phenylcarbimide or phenylthiocarbimide) were also prepared; of these, the last melts at 227—228°, the others remain unmelted at 300°. When amidomethylazimidobenzene hydrobromide (20 grams) is heated with methylic alcohol (22 grams) for 16 hours at 130—135°, yellow dimethylamidomethylazimidobenzene methobromide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N}_3\text{Me} \cdot \text{MeBr}$, melting at 262°, is obtained; the corresponding *chloride* and yellow *picrate* melt at 205° and 169—170°. From the mother liquor of the bromide, by displacing the bromine by chlorine and adding mercuric chloride, a trimethylmethylazimido-

phenylium compound, $\text{HHgCl}_3 \cdot \text{MeCl} \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N}_3\text{Me}$, melting at 195° , is obtained. If a relatively much smaller amount of methylic alcohol (0.8 gram per 5 grams of the hydrobromide) is used in the methylation, only a small quantity of a yellowish-brown nitroso-compound melting and decomposing at $150.5-151.5^\circ$ (presumably methylazimidophenylmethylnitrosamine, $\text{NO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_3 \cdot \text{N}_3\text{Me}$), is formed when the product is treated with nitrous acid, so that the methylation probably begins with the addition of MeBr to the N_3Me group. *Dimethylamidomethylazimidobenzene* (methylazimidodimethylaniline), $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N}_3\text{Me}$, is obtained by heating the above-mentioned methobromide with ammonia of sp. gr. = 0.91 for 9–10 hours at $180-185^\circ$, extracting with ether, evaporating the extract, dissolving the residue in hydrochloric acid, and precipitating with mercuric chloride; it melts at 90° , the *mercurochloride* (with $\text{HCl}, \text{HgCl}_2$) at $174-175^\circ$, and the *picrate* (with $2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$) at $180-181^\circ$. By dissolving the base in hydrochloric acid, cooling the solution, and adding sodium nitrite, a nitro-derivative is obtained, *methylazimidonitrodimethylaniline*,



This is orange-red, and melts at 141° ; dilute aqueous potash liberates dimethylamine, and acetic acid precipitates from the solution a yellowish-brown nitroso-compound melting at 191° , which is presumably methylazimidonitrophenylmethylnitrosamine. Reduction with zinc dust and acetic acid converts the nitro-compound into *methylazimidoamidodimethylaniline*, $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{NMe}_2) \cdot \text{N}_3\text{Me}$, the *zincchloride* of which (with $\text{HCl}, \text{ZnCl}_2$) melts at 276° ; this base gives the phenazine reaction, from which it follows that the amido- and di-methyl-amido-groups must be in the ortho-position relatively to each other.

Both amidomethylazimidobenzene and its dimethyl-derivative yield colouring matters with diazobenzenesulphonic acid; in this respect, the substitution of methyl for imido-hydrogen in amidoazimidobenzene has had no effect. C. F. B.

Intramolecular Rearrangement of Isoaldoxime Ethers. By CARL NEUBAUER (*Annalen*, 1897, 298, 187–201).—It has been shown that when the nitrogen benzyl ether of paranitrobenzaloxime, in alcoholic solution, is heated with a very small quantity of sodium ethoxide, a part undergoes conversion into the nitrogen paranitrobenzyl ether of benzaloxime, the action being reversible; a similar change on the part of the benzyl ether of metanitroisobenzaloxime is, however, not reversible, whilst the benzyl ether of isonisaloxime is indifferent to the conditions described. The author has prepared other isaldoxime ethers, and submitted them to the influence of alcoholic sodium ethoxide.

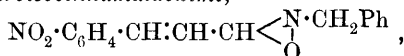
Benzylisocinnamaloxime, $\text{CHPh} : \text{CH} : \text{CH} < \text{N} \begin{array}{c} \text{N} \\ \text{O} \end{array} \text{CH}_2\text{Ph}$, is obtained

by heating cinnamaldehyde with β -benzylhydroxylamine hydrochloride (1 mol.) and sodium hydrogen carbonate in alcohol; it crystallises from dilute alcohol in lustrous, light yellow leaflets, and melts at 130° .

Benzylorthochlorisobenzaldoxime, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\begin{smallmatrix} \text{N}\cdot\text{CH}_2\text{Ph} \\ \text{O} \end{smallmatrix}$, crystallises from petroleum in cubes, and melts at 86° .

Benzylorthonitroisobenzaldoxime, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\begin{smallmatrix} \text{N}\cdot\text{CH}_2\text{Ph} \\ \text{O} \end{smallmatrix}$, crystallises from very dilute alcohol in yellowish needles, and melts at $125-126^\circ$.

Benzylmetanitroisocinnamaldoxime,

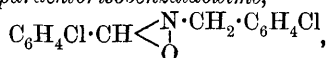


separates from benzene in yellow, lustrous leaflets, and melts at 123° .

Benzylparahydroxyisobenzaldoxime, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\begin{smallmatrix} \text{N}\cdot\text{CH}_2\text{Ph} \\ \text{O} \end{smallmatrix}$, crystallises from dilute alcohol in long, colourless needles, and melts at 203° .

β -*Diparachlorodibenzylhydroxylamine*, $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2)_2\text{N}\cdot\text{OH}$, is obtained by heating parachlorobenzyl chloride (2 mols.) in alcohol with hydroxylamine hydrochloride and sodium carbonate in a reflux apparatus; it crystallises from alcohol in white needles, and melts at $121-122^\circ$.

Parachlorobenzylparachlorisobenzaldoxime,



is prepared from dichlorodibenzylhydroxylamine by oxidation with potassium dichromate and glacial acetic acid; it crystallises from alcohol in lustrous, white plates, and melts at 141° .

β -*Parachlorobenzylhydroxylamine*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{OH}$, obtained by passing steam into a solution of parachlorobenzylparachlorisobenzaldoxime in 20 per cent. hydrochloric acid, crystallises from light petroleum in beautiful, long needles, and melts at $87-88^\circ$. The *hydrochloride* melts at $165-166^\circ$.

Parachlorobenzylisobenzaldoxime, $\text{CHPh}\begin{smallmatrix} \text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Cl} \\ \text{O} \end{smallmatrix}$, crystallises from dilute alcohol in rhombic leaflets, and melts at $125-126^\circ$.

Benzylparachlorisobenzaldoxime, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\begin{smallmatrix} \text{N}\cdot\text{CH}_2\text{Ph} \\ \text{O} \end{smallmatrix}$, separates from dilute alcohol in long, prismatic needles, and melts at 121° .

Of the foregoing ethers, parachlorobenzylisobenzaldoxime and benzylparachlorisobenzaldoxime undergo molecular rearrangement.

A convenient method of preparing β -benzylhydroxylamine consists in heating a mixture of acetoxime and benzaldehyde (1 mol.) with an equal volume of 75 per cent. acetic acid in a reflux apparatus.

M. O. F.

Vinylideneoxanilide. By HANS VON PECHMANN (*Ber.*, 1897, 30, 2791—2794).—This substance, $\begin{smallmatrix} \text{CO}\cdot\text{NPh} \\ | \\ \text{CO}\cdot\text{NPh} \end{smallmatrix} > \text{C}\cdot\text{CH}_2$, which is formed when glyoxime-N-phenyl ether (*Abstr.*, 1897, i, 75) is heated with acetic anhydride, is more conveniently prepared by boiling oxanilide with

acetic anhydride and sodium acetate. It melts at 208—210°, decolorises permanganate immediately, and reacts with bromine at 0° in chloroform solution; in the latter case, however, hydrogen bromide is given off, and the product, which melts at 189° and decolorises permanganate, is *bromovinylideneoxanilide*, $C_3N_2Ph_2O_2 \cdot CHBr$. Alcoholic hydrochloric acid decomposes it into its components, whilst alcoholic potash hydrolyses it to oxalic acid and ethenyldiphenylamidine, $NPh \cdot CMe \cdot NHPh$. Bromovinylideneoxanilide is hydrolysed by alcoholic potash to oxanilic acid, aniline, a little oxanilide, and presumably bromacetic acid.

C. F. B.

Dyeing with "Substantive" Dyes. By LÉO VIGNON (*Compt. rend.*, 1897, 125, 357—360).—As the result of various experiments, the author arrives at the following conclusions. The fixation of substantive dyes (for example, congo-red) on cotton is a chemical process, since the chemical composition of the dyes influences the fixation to a remarkable degree. Diamines (with the exception of orthophenylenediamine) and hydrazines are readily fixed, even when the amido-groups are substituted. Diphenyl, azobenzene, ammonia, hydroxylamine, and aromatic amines are not fixed. The dyeing of cotton is due to the presence of the group $=N \cdot R \cdot N=$ or simply $=N \cdot N=$; it is probable that the fixing of the dye is due to the conversion of triad nitrogen into pentad, by the addition of cellulose molecules. This conclusion is supported by the fact that benzidine and tetramethylbenzidine, in both of which nitrogen is tervalent, can be fixed. But tetramethylbenzidine dimethyliodide, $C_6H_{12}(NMe_3I)_2$, in which nitrogen is quinquevalent, can not.

J. J. S.

Some Organic Compounds containing Inorganic Radicles. By C. A. AUGUST MICHAELIS (*Ber.*, 1897, 30, 2821—2822. Compare the following abstracts).—The radicles $SeCl_2$ and $TeCl_2$ can readily be introduced into various classes of organic compounds, the derivatives of the ketones, such as $(Ph \cdot CO \cdot CH_2)_2SeCl_2$ being of special interest. It is worthy of remark that the compounds of bismuth in which the metal is quinquevalent are more stable than those in which it is tervalent.

A. H.

Organic Selenium Compounds. By C. A. AUGUST MICHAELIS and FRANZ KUNCKELL (*Ber.*, 1897, 30, 2823—2828. Compare the foregoing abstract, and Abstr., 1895, i, 341).—*Selenonaphthyl methyl ether*, $(MeO \cdot C_{10}H_6)_2Se$, obtained by adding selenyl chloride to an ethereal solution of α -naphthyl methyl ether, forms a crystalline mass melting at 138°. The corresponding β -compound crystallises in needles, melting at 162°. *Seleno- α -naphthyl ethyl ether* forms small, lemon-yellow needles, melting at 149°, whilst the β -compound crystallises in pure white needles, and melts at 176°. Selenyl chloride also reacts with phenols to form similar compounds. *Selenophenol*, $Se(C_6H_4 \cdot OH)_2$, forms a brittle, yellow mass soluble in alkalis. *Seleno- β -naphthol* crystallises in small plates, which have a reddish lustre and melt at 186°. *Selenylresorcinol*, $SeO[C_6H_3(OH)_2]_2$, has only been obtained in the form of a reddish-brown, brittle mass, which melts between 170° and 173°.

Selenium tetrachloride readily reacts with ketones to form compounds which still contain 2 atoms of chlorine. *Dichroselenoacetone*

$(\text{COMe}\cdot\text{CH}_2)_2\text{SeCl}_2$, crystallises in white needles, which melt at 82° and emit a vapour which attacks the mucous membrane. It decomposes when kept, and is decomposed by boiling water, with separation of selenium. *Dichloroselenoacetophenone*, $(\text{COPh}\cdot\text{CH}_2)_2\text{SeCl}_2$, which is much more stable than the acetone derivative, crystallises in white needles; these melt at 122° , and can be preserved without undergoing any alteration. With dilute aqueous soda, this compound yields acetophenone and selenious acid, but when warmed with more concentrated soda, selenium is deposited. With phenylhydrazine, it yields a resinous mass.

A. H.

Organic Tellurium Compounds. By E. Rust (*Ber.*, 1897, 30, 2828—2834. Compare the foregoing abstracts).—Tellurium tetrachloride crystallises from ether in long yellow needles containing 1 mol. of the solvent. *Dichlorotelluroanisole*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$, obtained by the action of the tetrachloride on anisole, crystallises in small, yellow needles melting at 190° . When its solution in hydrochloric acid is evaporated with platinum chloride, yellowish-brown needles of the *platinochloride*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2\cdot\text{PtCl}_4$, are obtained. *Dihydroxytelluroanisole*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{Te}(\text{OH})_2$, is obtained as an amorphous, white powder on dissolving the dichloro-compound in dilute aqueous soda and acidifying with acetic acid; when heated, it decomposes without melting and dissolves both in acids and alkalis. The *oxide*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{TeO}$, appears to be formed when the hydroxide is gently heated, but has not been obtained pure. *Dibromotelluroanisole*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{TeBr}_2$, prepared by dissolving the hydroxide in hydrobromic acid, crystallises in yellow needles, and melts at 183.5° . *Di-iodotelluroanisole*, crystallises in reddish-brown, lustrous plates, melting at 170° , whilst the *nitrate* forms colourless, compact crystals melting at 127 — 128° , and is soluble in water. *Dichlorotellurophenetole*, $(\text{OEt}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$, crystallises in yellow needles, which melt at 185° . The *dihydroxy*-derivative is an amorphous, white powder; the *dibromo*-derivative crystallises in yellow needles melting at 183° . The *nitrate* crystallises in colourless plates, and melts at 120° . Tellurium tetrachloride combines with phenol in ethereal solution to form an *additive* compound, $\text{TeCl}_4\cdot 2\text{PhOH}$; this is a yellow, crystalline mass, which becomes brown at 182 — 183° . When the tetrachloride is heated with phenol, hydrogen chloride is evolved, but tellurium separates out. No crystalline products could be obtained by the action of the tetrachloride on naphthol, but with resorcinol, reaction takes place, and *dichlorotelluroresorcinol*, $[\text{C}_6\text{H}_3(\text{OH})_2]_2\text{TeCl}_2$, is produced; this forms small, yellow crystals melting at 188 — 189° . The corresponding *dihydroxy*-compound is a white, amorphous powder. Like the corresponding selenium compound, tellurium tetrachloride readily reacts with ketones. *Dichlorotelluroacetophenone*, $(\text{COPh}\cdot\text{CH}_2)_2\text{TeCl}_2$, crystallises in slender, yellowish-white needles, which melt at 186 — 187° ; potassium permanganate converts it into tellurous acid and chloracetophenone. The tetrachloride does not react with bromacetophenone. *Dichlorotelluroanisyl methyl ketone*, $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3)_2\text{TeCl}_2$, crystallises in small, white needles melting at 190° . *Dichlorotelluroparatolyl methyl ketone* forms small, white needles melting and becoming green at 200° .

A. H.

Antimony Derivatives of Anisoil and Phenetoil. By CARL LÖLOFF (*Ber.*, 1897, 30, 2834—2843).—*Trianisylstibine*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_3\text{Sb}$, may be prepared by the action of sodium on a mixture of bromanis-oil and antimony trichloride dissolved in benzene, or by the action of bromanis-oil on an alloy of antimony and sodium. It crystallises in well-developed, colourless rhombohedra melting at $180\cdot5$ — 181° ; hot concentrated hydrochloric acid converts it into anisoil and antimony trichloride. Alcoholic mercuric chloride added to its solution in chloroform, produces a white, crystalline precipitate of the compound, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_3\text{Sb}\cdot\text{HgCl}_2$, which decomposes without melting at 285° ; when this is boiled with alcohol, it yields paranisylmercuric chloride, $\text{HgCl}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ (Michaelis and Rabinerson, *Abstr.*, 1890, 1269). *Trianisylstibine dichloride*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_3\text{SbCl}_2$, is formed when alcoholic cupric chloride is added to a chloroform solution of the stibine, cuprous chloride being also formed. It crystallises from benzene in large prisms with 1 mol. of the solvent; these melt at 82 — 83° , whilst the pure substance melts at 116 — 117° . *Trianisylstibine dibromide*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_3\text{SbBr}_2$, formed by the direct union of the stibine with bromine, crystallises in thin plates melting at 123° ; it also separates from benzene in prisms containing 1 mol. of the solvent and melting at 81 — 82° . The *di-iodide* forms yellow, monosymmetric plates, which melt at 116° ; the *nitrate*, which can be prepared by the action of silver nitrate on the bromide in alcoholic solution, crystallises in short, slender needles, which melt and decompose at 217° . *Trianisylstibine oxide*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_3\text{SbO}$, obtained by the action of alkalis on the halogen compounds, forms crystalline crusts melting at 191° ; acids convert it into the salts described above.

Chlorine acts energetically on the stibine, resinous products being formed. When the chlorination is effected in a well-cooled chloroform solution, however, *dichloranisylstibine trichloride*, $(\text{OMe}\cdot\text{C}_6\text{H}_2\text{Cl}_2)_3\text{SbCl}_3$, is produced, which forms colourless crystals melting at $184\cdot5^\circ$; tri-chloranis-oil, $[\text{OMe}\cdot\text{Cl}_3 = 1 : 2 : 4 : 6]$, is also produced in the reaction. *Dichloranisylstibic acid*, $(\text{OMe}\cdot\text{C}_6\text{H}_2\text{Cl}_2)_3\text{SbO}\cdot\text{OH}$, formed by the action of water on the foregoing compound, is a white, amorphous powder which melts and decomposes at 228 — 229° , and is insoluble in water and alcohol, but dissolves in aqueous soda and in alcoholic hydrogen chloride.

Triphenetylstibine, $(\text{OEt}\cdot\text{C}_6\text{H}_4)_3\text{Sb}$, crystallises in nodular aggregates of needles melting at 82 — 83° , and is decomposed by hydrochloric acid into phenetoil and antimony trichloride. The *mercurochloride*, $(\text{OEt}\cdot\text{C}_6\text{H}_4)_3\text{Sb}\cdot\text{HgCl}_2$, is a white, crystalline, insoluble powder which decomposes at 225° . *Paratriphenetylstibine dichloride* crystallises with difficulty and melts at 84° ; the *dibromide* crystallises in slender, asbestos-like needles melting at 110 — 111° ; the *di-iodide* in prisms melting at 121 — 122° , whilst the *nitrate* separates in crystalline crusts which melt at 151 — 152° . The corresponding oxide could not be obtained. Chlorine produces a mixture of chlorinated diphenetylstibine chlorides, which are decomposed by water. A. H.

Some Aromatic Bismuth Compounds. By ARNOLD GILLMEISTER (*Ber.*, 1897, 30, 2843—2850. Compare the foregoing abstracts).—Bismuthtriphenyl does not appear to form a di-iodide, since when it is

acted on by iodine, or when the chloride is treated with potassium iodide, *bismuthodiphenyl iodide*, Ph_2BiI , is produced; this crystallises in yellow needles melting at 133° , and is decomposed by alcohol, bismuth-oxyiodide being formed. Bismuthotriphenyl is completely decomposed by a mixture of nitric and sulphuric acids, whereas the dichloride and the nitrate can readily be nitrated. *Bismuthodinitrotriphenyl dinitrate*, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4)_2\text{PhBi}(\text{NO}_3)_2$, obtained by the action of nitric and sulphuric acids on the nitrate, crystallises in flat, lustrous, yellowish prisms, which explode feebly at about 150° . The corresponding *dichloride* is precipitated when hydrochloric acid is added to a solution of the nitrate in acetic acid; it crystallises in slender, white needles which melt at 136° , and detonate slightly when rapidly heated. *Orthobismuthotritolyl*, $\text{Bi}(\text{C}_6\text{H}_4\text{Me})_3$, obtained by the action of orthobromotoluene on an alloy of bismuth with sodium, crystallises in colourless rhombohedra, which are isogonous with those of calc spar and melt at 128.5° ; it is decomposed by hot concentrated hydrochloric acid, toluene being formed. The *dichloride*, $(\text{C}_6\text{H}_4\text{Me})_3\text{BiCl}_2$, formed by the direct combination of bismuthotritolyl with chlorine, forms white, rhombic crystals melting at 160° . The *dibromide* crystallises in yellow needles which melt at 125° , and gradually decompose on exposure to the air. The *nitrate* also forms rhombic crystals, and decomposes suddenly when heated.

Parabismuthotrixylyl, $(\text{C}_6\text{H}_3\text{Me}_2)_3\text{Bi}$, forms snow-white, matted needles which melt at 194.5° and are decomposed when heated with hydrochloric acid; the *dichloride* melts at 167.5° and the *dibromide* at 130° . *Parabismuthotricumyl* forms lustrous, rhombohedral tablets melting at 159° ; the *dichloride* melts at 208° , and the *dibromide* at 150° . Pseudocumene and mesitylene derivatives could not be obtained. *Parabismuthotrianisyl*, $(\text{OMe} \cdot \text{C}_6\text{H}_4)_3\text{Bi}$, was obtained in small quantity from bromanisole in the usual way. It forms lustrous cubes, melts at 190° , and is at once decomposed in the cold by hydrochloric acid. This compound is accompanied by *paradianisyl*, $(\text{OMe} \cdot \text{C}_6\text{H}_4)_2$, which crystallises in colourless, lustrous plates melting at 172° , and readily sublimes. Hydriodic acid converts it into paradiphenol. *Bismuthotrianisyl dibromide* crystallises in yellow needles melting at 103° , and is very stable. Chlorine converts the trianisyl compound into *bismuthotrichloranisyl dichloride*, $(\text{OMe} \cdot \text{C}_6\text{H}_3\text{Cl})_3\text{BiCl}_2$, which melts at 133° . *Parabismuthotriphenetyl* forms monosymmetric prisms melting at 73° . No halogen derivatives could be obtained. A. H.

Halogen Derivatives of Phenyl Methyl Ketone. By A. COLLET (*Compt. rend.*, 1897, 125, 717—719).—Chloroacetic chloride and bromoacetic chloride in presence of aluminium chloride and carbon bisulphide act readily on chlorobenzene and bromobenzene, yielding dichloro-, dibromo-, or chlorobromo-derivatives of phenyl methyl ketone. *Parachlorophenyl chloromethyl ketone* melts at 101 — 102° . Gautier obtained the same compound by the action of chlorine on parachlorophenyl methyl ketone. *Parabromophenyl chloromethyl ketone* melts at 116 — 117° ; *parachlorophenyl bromomethyl ketone* at 96 — 96.5° ; and *parabromophenyl bromomethyl ketone* at 109 — 109.5° .

All these derivatives crystallise in slender, colourless needles and

dissolve in alcohol, especially on heating. When oxidised, the acetyl group is removed and parachloro- or parabromo-benzoic acid is obtained.

C. H. B.

Ethylc Quinoltetracarboxylic Acid from Ethylc Acetone-dicarboxylic Acid. By HANS VON PECHMANN and LUDWIG WOLMAN (*Ber.*, 1897, 30, 2569—2571).—After ethylc diacetylsuccinic acid had been synthesised by the action of iodine on the sodium compound of ethylc acetoacetate, a similar experiment was tried with the disodium compound of ethylc acetonedicarboxylate, and it was found that, under the conditions of experiment, 2 mols. of the disodium compound condensed, forming 4 mols. of sodium iodide and the corresponding diketohexamethylene compound. The latter, however, is oxidised at the moment of its formation by the free iodine present, and converted into ethylc quinoltetracarboxylic acid melting at 133—133·5°.

J. F. T.

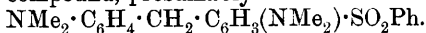
Decomposition of Alkyl-sulphonates by Water, Acids, and Salts. By J. H. KASTLE, PAUL MURRILL, and JOS. C. FRAZER (*Amer. Chem. J.*, 1897, 19, 894—901).—In continuation of Kastle and Murrill's previous work on the saponification of alkyl sulphonates by alcohols (*Abstr.*, 1895, i, 370), the authors have determined the velocity of the decomposition of ethylc parabromobenzenesulphonate by water, alcohol, acids, and salts. In the case of water and aqueous solutions, complete mixture was effected by adding acetone. The progress of the action was determined from time to time by titrating with standard alkali, and in the case of the halogen acids and salts it was found necessary also to estimate the quantity of halogen which had not entered into reaction, by means of silver nitrate, since not only is the sulphonate decomposed by the water, but ethylc haloid is also formed. A. S. Loevenhart has obtained ethylc iodide in quantity by the action of potassium iodide on ethylc parabromobenzenesulphonate in solution in alcohol or acetone.

The velocity of the action in the case of water was found to be 3·5 times as great as for ethylc alcohol, whilst acids and salts were found to react much more rapidly than water alone. Rise of temperature causes a great increase in the velocity of decomposition, hydrochloric acid, for instance, at 98° effects as much decomposition in 20 minutes as it does in 10 days at the ordinary temperature. In some cases, the distribution of decomposition between the acid and the water was independent of temperature; with hydrochloric acid at the ordinary temperature, 72 per cent. of the sulphonate was decomposed by the acid and 16 per cent. by the water, whilst at 98°, 71 per cent. was decomposed by the acid and 16 by the water. Hydrochloric, hydrobromic, and hydriodic acid bring about the same amount of decomposition, and this is the case also with magnesium chloride and calcium chloride.

E. W. W.

Benzenesulphinic Acid as a Reagent. By OSCAR HINSBERG (*Ber.*, 1897, 30, 2803—2805).—Benzenesulphinic acid (which has already been shown to unite with substances of quinonoid structure, forming sulphones; *Abstr.*, 1896, i, 684) unites also with tetramethyldi-

amidobenzhydrol in dilute hydrochloric acid solution (when the latter substance must be formulated $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2\text{Cl}$), yielding an additive compound, presumably



This melts at 194° , is stable to acids and alkalis, and is oxidised by potassium permanganate and dilute sulphuric acid to a ketone that contains sulphur, presumably $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{NMe}_2) \cdot \text{SO}_2\text{H}$.

C. F. B.

Paratoluenesulphinic Acid. By F. ARTHUR HÄLSSIG (*J. pr. chem.*, 1897, **56**, 213—241. Compare next abstract, and Abstr., 1896, i, 684).—When ammonia is passed into a solution of paratoluenesulphinic acid in alcoholic or ethereal solution, the *ammonium* salt of the acid is obtained, which crystallises from alcohol in colourless needles melting and decomposing at 175° . If the reaction takes place in benzene solution, the ammonium salt of paratoluenesulphonic acid and paratoluenedisulphoxide are formed. Presumably, the ammonia acts first as a reducing agent, whereby 2 molecules of the sulphinic acid each give up a hydrogen and an oxygen atom, and the two SO groups become changed to $\text{SO}_2 \cdot \text{S}$, a third molecule becoming oxidised to the sulphonic acid.

Aromatic amines react with paratoluenesulphinic acid, giving salts which, when strongly heated, yield blue to red violet resins, from which the colouring matters could not be isolated. The *aniline* salt crystallises in colourless needles melting at 118° ; the *orthotoluidine* salt in colourless needles melting at 124° ; the *paratoluidine* salt in needles melting at 140° , and the *metaxylydene* salt in white needles melting at 129.5° . With *phenylhydrazine*, a salt is obtained as colourless, asbestos-like needles melting at 159 — 160° with decomposition; and with *hydrazine hydrate*, a salt as glistening leaflets melting partially at 107° , and decomposing entirely at 140° .

Phenylparatoluenesulphazide, $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{NHPh}$, is prepared by the action of phenylhydrazine on paratoluenesulphonic chloride; it crystallises from alcohol in beautiful needles melting and decomposing at 155° . When treated with sodium hydroxide, it is converted into benzene, nitrogen, water, and sodium paratoluenesulphinate; at the same time, a red, crystalline substance melting at 65° is obtained, but in quantity too small for further investigation. The same sulphazide is also produced together with paratoluenedisulphoxide when paratoluenesulphinic acid is acted on with phenylhydrazine hydrochloride.

By the action of hydrazine hydrochloride on paratoluenesulphinic acid, paratoluenedisulphoxide is obtained, together with a substance crystallising from alcohol in clear needles and melting at 180.5° with decomposition. Its aqueous solution reacts feebly acid, and reduces ammoniacal silver nitrate at ordinary temperatures. It yields a *benzoyl* derivative crystallising from alcohol in needles melting and decomposing at 209.5° , but the constitution of this substance has not so far been satisfactorily determined. Phenylmethylhydrazine and paratoluenesulphinic acid give rise to a salt crystallising from alcohol in silken needles melting at 126° ; this, when treated with hydrochloric acid, is transformed into a substance of the composition $\text{C}_{28}\text{H}_{34}\text{S}_2\text{O}_3\text{N}_4$. Neither by this re-

action nor by the action of phenylmethylhydrazine on paratoluenesulphonic chloride could the corresponding sulphazide be obtained.

Free hydroxylamine reacts with paratoluenesulphinic acid, giving rise to paratoluenesulphonamide, and the hydroxylamine salt of the acid as an intermediate product. The action with β -dibenzylhydroxylamine is complex; the products are benzaldehyde, paratoluenedisulphoxide, benzylisobenzaldoxime, *paratoluenesulphinic acid β -benzylhydroxylamine* forming mother-of-pearl, glistening leaflets melting at 176° , and the *β -dibenzylhydroxylamine* salt as small crystals melting at 156° .

By melting acetoxime or α -benzaldoxime with paratoluenesulphinic acid, the ammonium salt of the acid and paratoluenesulphonamide are produced; but if the action take place in acetic acid solution, with acetoxime, paratoluenedisulphoxide and ammonium paratoluenesulphonate are formed, and with benzaldoxime a *condensation* product insoluble in alcohol, ether, and benzene, and soluble only with decomposition in acetic acid; it melts at 124° , and is converted by dilute alkalis into benzaldehyde, paratoluenesulphonamide, and paratoluenesulphinic acid.

A. W. C.

Derivatives of Paratoluenesulphinic Acid. By ERNST VON MEYER (*J. pr. chem.*, 1897, **56**, 272. Compare preceding abstract, and Abstr., 1896, i, 684).—A preliminary note on the compounds formed by the action of certain diazo-compounds on paratoluenesulphinic acid. The *substance*, $\text{N}_2\text{Ph}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, forms beautiful, yellow crystals melting at 94.5° . When acted on by aniline, methyl-, or dimethylaniline or quinoline in alcoholic solution, it is converted into a *substance* of the composition $\text{C}_{20}\text{H}_{20}\text{S}_2\text{O}_4\text{N}_2$, which is probably *diparatolylsulphone phenylhydrazine*; this forms white needles melting at 198° .

A. W. C.

A Transformation of Tetrahydropyrone Derivatives. By PAWEŁ IW. PETRENKO-KRITSCHENKO and D. PLOTNIKOFF (*Ber.*, 1897, **30**, 2801—2803).—When acetonedicarboxylic acid is mixed with three times the quantity of benzaldehyde, the product shaken with dilute soda, and the solution, after being freed from excess of benzaldehyde by extraction with ether, is acidified, *diphenyltetrahydropyromedicarboxylic acid*, $\text{CO} \begin{array}{c} \text{CH}(\text{COOH})\cdot\text{CHPh} \\ \text{CH}(\text{COOH})\cdot\text{CHPh} \end{array} \text{O}$, separates as a semi-solid mass. It gradually loses carbonic anhydride, and the product is *diphenyltetrahydropyrone*, $\text{CO} \begin{array}{c} \text{CH}_2\cdot\text{CHPh} \\ \text{CH}_2\cdot\text{CHPh} \end{array} \text{O}$; this melts at 131° . When its alcoholic solution is warmed with a few drops of hydrochloric acid, dibenzylideneacetone, $\text{CO}(\text{CH}:\text{CHPh})_2$, is formed.

C. F. B.

Action of Tetrazodiphenyl Chloride on Benzene. By E. CASTELLANETA (*Ber.*, 1897, **30**, 2799—2801).—Tetrazodiphenyl chloride, $\text{Cl}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{Cl}$, is prepared by dissolving benzidine in absolute alcohol, passing in gaseous hydrogen chloride, adding amylic nitrite at 5° , and then ether; it explodes at 106 — 108° or when struck, and keeps well in the dry state. When it is heated on the water bath with excess of benzene and a little aluminium chloride, it yields a mixture of *parachloroparadiphenylbenzene*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}_6\text{H}_4\text{Ph}$, melting at 220 — 220.5° , with *paradichlorodiphenyl*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}_6\text{H}_4\text{Cl}$, the latter of

which is rather more soluble in alcohol than the first ; no biphenyl-diphenyl, $C_6H_4Ph \cdot C_6H_4Ph$, is formed. C. F. B.

Aromatic Hydroxyketones. By EMILIO NOELTING and ALFRED MEYER (*Ber.*, 1897, **30**, 2590—2595).—2 : 3 : 4 : 3' : 4'-*Pentahydroxybenzophenone*, $C_6H_2(OH)_3 \cdot CO \cdot C_6H_3(OH)_2$, obtained by heating protocatechuic acid with pyrogallol and zinc chloride at 140—145°, crystallises with $2H_2O$ in slender, light yellow needles, and melts when dry at 192—193°. Concentrated sulphuric acid converts it into protocatechuic acid and decomposition products of pyrogallol.

An *isomeric* compound, $[(OH)_5 = 3 : 4 : 5 : 3' : 4']$, is produced when gallic acid is heated with catechol and zinc chloride ; it also crystallises in light, yellow needles with $2H_2O$, but melts at 266° ; like its isomeride, it yields protocatechuic acid when heated with sulphuric acid. This reaction shows the constitution of the two compounds.

2 : 4 : 3' : 4'-*Tetrahydroxybenzophenone*, $CO[C_6H_3(OH)_2]_2$, obtained from protocatechuic acid and resorcinol, forms brownish-yellow crystals containing $2H_2O$, and melts at 199°. 2 : 3 : 4-*Trihydroxyphenyl 3-hydroxy-β-naphthyl ketone*, $OH \cdot C_{10}H_6 \cdot CO \cdot C_6H_2(OH)_3$, is prepared from β-hydroxynaphthoic acid and pyrogallol ; it forms small, yellow crystals melting at 287—289°. When heated with resorcinol and zinc chloride, β-hydroxynaphthoic acid yields a substance which is probably a mixture of the ketone with hydroxyxanthone formed from it by loss of water. Pentahydroxy- and tetrahydroxy-benzophenone have been previously described in the German Patent No. 72446, belonging to the Höchst company. A. H.

New Method of obtaining Colouring Matters of the Malachite-Green Series. By EMILIO NOELTING (*Ber.*, 1897, **30**, 2588—2590).—Benzanilide and its derivatives usually react with tertiary aromatic amines in presence of phosphorus oxychloride to form derivatives of dialkylamidobenzophenones. (German Patent, 41751). When, however, a hydroxy-group is present in the ortho-position in the benzoic acid residue the reaction takes another course, and a compound of the malachite-green series is produced. Thus salicylanilide and dimethylaniline react to form a green *colouring matter* which on reduction yields the leuco-base obtained by O. Fischer from salicylaldehyde and dimethylaniline (*Abstr.*, 1882, 392). Orthocresotic anilide yields a similar *compound*, whereas the anilides of meta- and para-hydroxybenzoic acid and of orthonitro- and orthamido-benzoic acid yield no compound of this class. A green colouring matter is also formed from the anilide of orthohydroxynaphthoic acid. A. H.

Paradinitrodibenzylsulphonic Acid. By CHRISTOPH RIS and CARLSIMON (*Ber.*, 1897, **30**, 2618—2620).—Sodium paradinitrodibenzylsulphonate can readily be prepared by the action of aqueous soda and sodium hypochlorite on sodium paranitrotolueneorthosulphonate ; it crystallises in colourless needles, and deflagrates at a high temperature. Alkalis convert it into yellow substances, and it appears probable that the yellow substance described by Bender (*Abstr.*, 1895, i, 287) as potassium paradinitrodibenzylsulphonate is in reality such a decomposition product. A. H.

Anilineazo- α -Naphthol. By OTTO N. WITT and JENS DEDICHEN (*Ber.*, 1897, 30, 2655—2667. Compare Abstr., 1894, i, 606).—In many respects the behaviour of anilineazo- α -naphthol is inconsistent with the view that it is the exact analogue of hydroxyazobenzene. Its resistance to ordinary methods of alkylating phenols, for instance, and the pronounced basic character of the colouring matter and its ethers, serve to differentiate it from the type in question.

The general method of preparing azo-colouring matters is not the most suitable for the production of anilineazo- α -naphthol, as the unmodified process gives rise also to a disazo-compound; this bye-product is not formed, however, if the operation is carried out in alcoholic solution. An ice-cold solution of diazobenzene chloride, prepared from 93 grams of aniline dissolved in 200 c.c. of concentrated hydrochloric acid and 250 c.c. of water, is added to a cooled solution of 155 grams of α -naphthol in 2000 c.c. of alcohol, anilineazo- α -naphthol hydrochloride being slowly deposited from the liquid; the azo-compound is obtained by dissolving the hydrochloride along with potassium acetate in boiling glacial acetic acid, from which it separates in reddish-brown crystals with green reflex. It melts at 206° . The potassium derivative forms large, reddish-brown crystals, with feeble metallic lustre.

The compound, $C_{32}H_{22}N_4O_2$, arising from elimination of two hydrogen atoms from 2 molecules of anilineazo- α -naphthol, is prepared by the action of oxidising agents such as ferric chloride and potassium dichromate, which when added to a solution of the potassium derivative, precipitate a mixture of unaltered colouring matter and the product of its oxidation; it is also obtained by the action of nitrosodimethylaniline, and by protracted treatment with boiling glacial acetic acid, in which it is insoluble. (Compare Fischer and Hepp, Abstr., 1892, 1476.) The substance forms deep red crystals, and melts and decomposes at 245 — 246° ; it is insoluble in ordinary media, and is devoid of basic properties. The solution in cold concentrated sulphuric acid is violet. The acetyl derivative crystallises from toluene in lustrous, orange-red, dichroic needles, and melts at 264 — 265° .

When the oxidation product from anilineazo- α -naphthol is reduced with tin and hydrochloric acid, diparamidonaphthol is produced, and when the hydrochloride of this base is oxidised with concentrated nitric acid, *dinaphthaquinone*, $C_{20}H_{10}O_4$, is obtained; it begins to decompose at 270° , and yields β -dinaphthyl when heated with zinc dust. The compound obtained by oxidising anilineazo- α -naphthol, therefore, has the constitution $NPh \cdot N \cdot C_{10}H_5(OH) \cdot C_{10}H_5(OH) \cdot N : NPh$.

It has been already stated that the new colouring matter forms a violet solution in concentrated sulphuric acid. If the liquid is gently heated it becomes blue, and when poured into water yields a dark brown precipitate, which becomes orange on treatment with soda; the compound, $C_{32}H_{20}N_4O$, obtained by this method is purified by precipitating its solution in phenol with alcohol, and subsequently crystallising from boiling xylene. It forms lustrous, orange-red crystals, and melts at 290 — 291° , when decomposition begins; the substance is insoluble in dilute acids and alkalis, and the solution in concentrated sulphuric acid is blue. Reduction converts it into the crystalline hydrochloride of a new compound.

M. O. F.

A General Reaction of Aromatic Quinones. II. By SIEGFRIED BLUMENFELD and PAUL FRIEDLÄNDER (*Ber.*, 1897, 30, 2563—2568. Compare Abstr., 1897, i, 473).—There are only two possible ways of formulating a substance formed by the condensation of a quinone with a phenol without elimination of water, for either the product is a hydroxy-derivative of a hydrocarbon, or the two rings are joined by means of oxygen, thus forming a hydroxy-derivative of an ether; for instance, the product of condensation of α -naphthaquinone with pyrogallol may be either a pentahydroxyphenylnaphthalene or a tetrahydroxyphenyl naphthyl ether. Since, on investigation, this compound was found to yield a tetracetyl derivative, the latter formula is evidently the correct one. 2:3-*Dihydroxyphenyl* 1:4-*dihydroxy-2-naphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_6H_3(OH)_2$, formed by the condensation of α -naphthaquinone with pyrogallol in glacial acetic acid solution, crystallises from the latter in pale grey needles melting and decomposing at 240—246°, the *tetracetyl* derivative crystallises from glacial acetic acid in colourless needles melting at 165—170°, whilst the *benzoyl* derivative forms white needles melting at 203—205°. *Dihydroxydi- α -naphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_{10}H_7$ [(OH)₂:O = 1:4:2], formed by the condensation of α -naphthaquinone with α -naphthol, crystallises in colourless needles melting at 240—245°, the *diacetyl* derivative crystallises from glacial acetic acid and softens at 240°, remaining, however, solid at 300°.

β -Naphthaquinone, on condensation with pyrogallol, yields 2:3-*dihydroxyphenyl* 1:2-*dihydroxynaphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_6H_3(OH)_2$, which, after recrystallisation, melts at 242—245°, and the *tetracetyl* derivative at 184—188°; with α -naphthol, β -naphthaquinone yields 1:2-*dihydroxydinaphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_{10}H_7$, which does not show a sharp melting point the *diacetyl* derivative melts at 220°. β -Naphthaquinone and resorcinol produces 3-*hydroxyphenyl* 1:2-*dihydroxynaphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_6H_4 \cdot OH$; this separates from its glacial acetic acid solution on dilution with water and melts at 236—240°. The *triacetyl* derivative melts at 169—170°.

Benzoquinone combines with α -naphthol and resorcinol, forming in the first case *trihydroxydiphenyl ether*, $C_6H_3(OH)_2 \cdot O \cdot C_6H_4(OH)$ [(OH)₂:O:OH = 1:4:1':3'], which crystallises with difficulty and yields a *benzoyl* compound which separates from alcohol in white needles melting at 188—191°.

J. F. T.

Isomeric Change of Dihydrocarvone into Carvenone. By IWAN L. KONDAKOFF and TH. GORBUNOFF (*J. pr. chem.*, 1897, 56, 248—257).—When a solution of $\Delta_{8,9}$ -dihydrocarvone in light petroleum is saturated with hydrogen bromide, the former substance is converted into carvenone. During the reaction a small amount of a bromo-derivative is formed, which, on treatment with zinc dust, is completely converted into the same carvenone, boiling at 232—233° at 758 mm. It has a sp. gr. = 0.921 at 20°/20°, and a refractive index $n_D = 1.47664$ at 20°, corresponding with a molecular refractive index of 46.63 (calculated 46.76).

Dihydrocarvone takes up the elements of hydrogen chloride when treated with the latter in acetic acid solution. The *chloroketone* formed boils at 155.5—157° at 15 mm.; has a sp. gr. = 1.0266 at 20°/20°; a

refractive index $n_D = 1.47877$, and is lævorotatory; $\alpha_D = -11.72$. When heated on the water bath for 2 hours with alcoholic soda, it loses completely the elements of hydrogen chloride, yielding *carone* boiling at $101-102^\circ$ at 15 mm. It has a sp. gr. = 0.9575 at $21^\circ/21^\circ$; a refractive index $n_D = 1.47664$, and is dextrorotatory; $\alpha_D = +174.36^\circ$. It is readily oxidised on treatment with potassium permanganate. The investigation is proceeding. A. W. C.

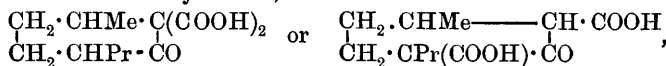
Menthonecarboxylic Acid and Menthonedicarboxylic Acid.

By GIUSEPPE ODDO (*Gazzetta*, 1897, **27**, ii, 97—116).—On treating menthone in absolute ethereal solution with sodium wire, a large part of the metal is rapidly dissolved, whilst the remainder only dissolves on prolonged ebullition; 1 atom of sodium requires $1\frac{1}{2}$ molecules of menthone for its solution. The liquid is saturated with carbonic anhydride, cooled with powdered ice, and the two layers separated; the ethereal solution, besides menthol and menthone, contains Beckmann's menthopinacone (Abstr., 1897, i, 248). On acidification with hydrochloric acid, the aqueous layer deposits an oil which can be extracted with ether; the ethereal solution, on evaporation, yields a mixture from which light petroleum extracts menthonecarboxylic acid, and leaves Brühl's menthonedicarboxylic acid (Abstr., 1892, 200). The petroleum extract is washed with sodium carbonate solution, and the latter acidified and extracted with ether; on evaporating this ethereal solution, menthomonocarboxylic acid is obtained.

Menthonecarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH} \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{CHPr} \cdot \text{CO} \end{array}$, is a heavy, colourless, nearly odourless oil, which yields menthone when heated with dilute sulphuric acid; it is sparingly soluble in water, and its solution turns violet with ferric chloride. The silver salt, $\text{C}_{10}\text{H}_{17}\text{O} \cdot \text{COOAg}$, is a flocculent, white precipitate. On treating the acid with sodium nitrite and acid at ordinary temperatures, isonitrosomenthone, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{C} \cdot \text{NOH} \\ | \\ \text{CH}_2 \cdot \text{CHPr} \cdot \text{CO} \end{array}$, is obtained, together with a reddish oil insoluble in alkalis, which is probably an orthodiketone of the constitution $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CHPr} \cdot \text{CO} \end{array}$; isonitrosomenthone is an oil which gives a yellow solution in alkalis. On reduction with zinc dust and acetic acid in dilute alcoholic solution, it yields menthoneamine, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH} \cdot \text{NH}_2 \\ | \\ \text{CH}_2 \cdot \text{CHPr} \cdot \text{CO} \end{array}$, as an oil smelling

like camphoramine; the hydrochloride crystallises in colourless prisms melting at $181-183^\circ$, and the platinochloride in red prisms which melt and decompose at $175-180^\circ$; apparently it yields thymol on heating.

Menthonedicarboxylic acid, which has the constitution



melts at $140-141^\circ$ with decomposition, not at 128.5° , as stated by Brühl (*loc. cit.*); when treated with diazobenzene chloride, it yields a compound which crystallises in dark-red crystals melting at $126-128^\circ$.

W. J. P.

Borneols and their Ethers. By JULES MINGUIN (*Compt. rend.*, 1896, 123, 1296—1298).—A method is described for separating dextro-borneol from lævoisoborneol in the mixture obtained by the reduction of camphor.

The author is of opinion that the phenomenon observed by Montgolfier on the etherification of a mixture of dextroborneol and lævoisoborneol, and on subsequent hydrolysis, namely, an increase in the dextrorotatory power, is not due to a partial conversion of the *l*-isoborneol into *d*-borneol, but is due to the fact that borneol is more readily etherified than isoborneol.

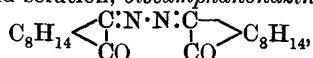
J. J. S.

Camphoquinone. By OTTO MANASSE and ERNST SAMUEL (*Ber.*, 1897, 30, 3157—3161. Compare *Abstr.*, 1897, i, 290).—The acid $C_{10}H_{16}O_3$ is obtained by dissolving finely-powdered camphoquinone in 15 parts of concentrated sulphuric acid, which is cooled and agitated during the process; after a short interval, the new substance is precipitated by pouring the liquid on to ice. It dissolves with great difficulty in cold water, but is soluble in 20 parts at 60° , separating from the solution in slender needles melting at 67 — 68° ; it contains $1H_2O$, which is removed in the desiccator or on exposure to a temperature of 50° , the anhydrous acid, which is very hygroscopic, melting at 97 — 98° . The acid is readily soluble in common organic solvents, excepting petroleum, from which it crystallises in long, slender needles melting at 97 — 98° ; it is monobasic in character, and exhibits the properties of an aldehyde or ketone, producing a metallic mirror when boiled with water and silver oxide, and developing a reddish-violet coloration with a sulphurous acid solution of magenta. It is somewhat stable towards potassium permanganate, and resists the action of boiling 50 per cent. sulphuric acid, but is readily oxidised by a solution of bromine in caustic soda. The *oxime* crystallises from chloroform in glistening leaflets, and melts at 163 — 164° ; it is readily soluble in acids and alkalis, but dissolves with some difficulty in water. The *phenylhydrazone* crystallises from dilute alcohol, and melts at 123 — 124° . The *semicarbazone* separates from alcohol as a microcrystalline powder and melts at 217 — 218° ; it dissolves readily in sodium carbonate, and the alcoholic solution reddens litmus.

When camphoquinone is exposed to the vapour of bromine, it is converted into the *compound*, $C_{10}H_{11}Br_2O_3$, which crystallises from benzene in lustrous prisms and melts at 197 — 198° . If bromination is carried out by adding bromine to the quinone until action ceases, and heating the product on the water bath, the *compound*, $C_{10}H_{12}Br_2O_3$, is produced; this, which crystallises from alcohol in long, lustrous needles, and melts at 137 — 138° , is not identical with π -dibromocamphoric anhydride.

M. O. F.

Camphor Compounds. By GIUSEPPE ODDO (*Gazzetta*, 1897, 27, ii, 117—131).—On heating camphoquinone with hydrazine hydrochloride in acetic acid solution, *biscamphanonazine*,



is obtained; it crystallises in colourless scales melting at 217 — 218° ,

is hydrolysed by fuming hydrochloric acid, and is identical with Angeli's azocamphanone (Abstr., 1895, i, 61).

Camphoquinone and hydriodic acid do not react in presence of red phosphorus at 115—125°, but at 150° the quinone is wholly converted into camphoric acid.

Bromocamphocarboxylic acid does not react with nitrous acid, but, under similar conditions, camphocarboxylic acid yields isonitroso-camphor (Abstr., 1893, i, 422); the bromo-acid should therefore contain the group -CBr(COOH)CO- and its ready conversion into bromocamphoric acid indicates that the bromine is attached to the same carbon atom in both acids.

α -Dibromocamphor is converted by sodium in boiling ethereal solution into monobromocamphor and a *dibromodizcamphor*, $\text{C}_{20}\text{H}_{30}\text{Br}_2\text{O}_2$; the latter crystallises in thin, white needles melting at 128—129°, and slowly decomposes with evolution of hydrogen bromide. Under similar conditions, β -dibromocamphor loses both bromine atoms, yielding a substance not yet examined.

In connection with the recent sitting of the Brunswick *Naturforscherversammlung* respecting the constitution of camphor, the author concludes that it is not yet possible to definitely state the constitution of this substance.

W. J. P.

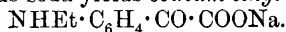
Conversion of Sulphocamphophenol into Dinitrocresol. By PAUL CAZENEUVE (*Compt. rend.*, 1896, 123, 1293—1295).—The compound previously obtained by the action of cold fuming nitric acid on the two sulphonated camphophenols and described as a tetranitro-derivative, $\text{C}_9\text{H}_8\text{O}(\text{NO}_2)_4(\text{SO}_2)(\text{OH})_2$ (Abstr., 1890, 1153), is now proved to be the dinitro-orthocresol $[\text{Me}:\text{OH}:(\text{NO}_2)_2 = 1:2:3:5]$ previously obtained by Nevile and Winther (*Trans.*, 1880, 631).

J. J. S.

Asymmetrical Alkylphenylhydrazines and some of their Derivatives. By C. A. AUGUST MICHAELIS (*Ber.*, 1897, 30, 2809—2821. Compare *Ber.*, 20, 2485).—The hydrochlorides of the asymmetrical alkylphenylhydrazines can readily be freed from phenylhydrazine hydrochloride by recrystallisation from chloroform or benzene, in which the latter is either insoluble or only sparingly soluble.

[With G. ROBISCH.]— α -Phenylethylhydrazine, $\text{NH}_2\cdot\text{NEtPh}$.—This is best prepared by the action of ethylic iodide on sodium phenylhydrazine (Abstr., 1889, 1158). It boils at 237° (corr.) and has a sp. gr. = 1.018 at 15°. It readily reacts with pyruvic acid to form a derivative which on heating with hydrochloric acid at 60° yields ethylindolecarboxylic acid (E. Fischer and O. Hess, *Ber.*, 17, 565). When this acid is heated at 190—195°, carbonic anhydride is evolved and 1'-ethylindole, $\text{C}_6\text{H}_4\text{<}\frac{\text{NEt}}{\text{CH}}\text{>CH}$, produced; the latter boils at 252—253° (corr.) and has a sp. gr. = 1.2563 at 15°. Its *picrate* crystallises in red needles and melts at 105°. *Dichlorethylloxindole*, $\text{C}_6\text{H}_4\text{<}\frac{\text{NEt}}{\text{CCl}_2}\text{>CO}$, obtained by the action of sodium hypochlorite on ethylindolecarboxylic acid, crystallises in yellowish prisms melting

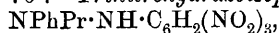
at 56°; *dibromethyloxindole* crystallises in yellow prisms melting at 95–96°. Water converts these halogen derivatives into ethyl- ψ -isatin, whilst aqueous soda yields *sodium ethyl- ψ -isatate*,



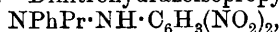
Ethylidioxindole, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NEt} \\ \text{CH}(\text{OH}) \end{smallmatrix} \right\rangle \text{CO}$, which can readily be prepared by the reduction of ethyl- ψ -isatin, crystallises in colourless prisms which soften at 143° and melt at 154–155°. 1'-*Ethylloxindole*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NEt} \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{CO}$, obtained by the reduction of dibromethyloxindole, crystallises in needles and is probably identical with that prepared by Baeyer and Comstock by the ethylation of oxindole (Abstr., 1883, 1130).

α -*Phenylpropylhydrazine*, $\text{NH}_2 \cdot \text{NPrPh}$, which boils at 247° (corr.) and has a sp. gr. = 0.9471, reduces Fehling's solution only very slowly in the cold and has an odour which resembles that of onions. 1'-*Propylindolecarboxylic acid*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NPr} \\ \text{CH} \end{smallmatrix} \right\rangle \text{C} \cdot \text{COOH}$, prepared in a similar manner to the ethyl compound, crystallises in white needles which melt at 170°, and then sublime and decompose into carbonic anhydride and 1'-*propylindole*; the latter is a colourless oil, which boils at 265° (corr.) and has a sp. gr. = 1.0559 at 15°. Its *picrate* forms red needles melting at 67°. *Dichloropropylloxindole* crystallises in yellowish needles melting at 67°; the *dibromo*-derivative forms prisms melting at 97°. 1'-*Propyl- ψ -isatin* crystallises in slender, bright-red needles melting at 72°. Barium propyl- ψ -isatate, obtained by the action of baryta water on dichloropropylloxindole, crystallises in silky, yellow needles. The β -*oxime*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NPr} \\ \text{C}(\text{N} \cdot \text{OH}) \end{smallmatrix} \right\rangle \text{CO}$, melts at 88°, and does not yield indigo when treated with ammonium sulphide. *Propylidioxindole* crystallises in yellow needles melting at 70°. *Propylloxindole* forms colourless crystals melting at 68–69°; bromine water added to its solution precipitates a bromine compound melting at 125°.

[With R. LMER].—*Isopropylphenylhydrazine*, $\text{NPh}(\text{CHMe})_2 \cdot \text{NH}_2$, prepared in a similar manner to the ethyl compound, boils at 236° and has a sp. gr. = 0.9588 at 15°. 1'-*Isopropylindolecarboxylic acid* melts at 183°, and the corresponding *indole* boils at 250° and forms a *picrate* which melts at 76°. *Trinitrohydrazoisopropylbenzene*,



formed by the action of picrylic chloride on isopropylphenylhydrazine in alcoholic solution, crystallises in brownish-red needles melting at 156°. It readily dissolves in aqueous alkalis, but no salts of it could be prepared. It is not acted on by mercuric oxide, and in this respect differs from trinitrophenylhydrazine, which is thereby converted into an azo-compound. *Dinitrohydrazoisopropylbenzene*,



obtained by the action of chlorodinitrobenzene on the hydrazine, crystallises in brownish-red needles which are insoluble in aqueous alkalis. α -*Phenylisobutylhydrazine* boils at 245°, and has a sp. gr. = 0.9633 at 15°. 1'-*Isobutylindolecarboxylic acid* crystallises in white, silky needles melting at 152°. 1'-*Isobutylindole* boils at 260°, and does

not form a crystallisable compound with picric acid. *Trinitrohydrazoisobutylbenzene*, $C_4H_9 \cdot NPh \cdot NH \cdot C_6H_2(NO_2)_3$, crystallises in red needles, melts at 105° , and dissolves in alkalis; the *dinitro*-derivative also crystallises in red needles and melts at 151° . *α -Phenylisoomylhydrazine* boils at 262° , and has a sp. gr. = 0.9680 at 15° . *1'-Isoamylindolecarboxylic acid* melts at 122° , whilst the corresponding *indole* boils at 276° and does not form a solid picrate. *Trinitrohydrazoisoomylbenzene* forms red needles melting at 58° , whilst the *dinitro*-compound crystallises in bright yellow needles, and melts at 104° . A. H.

4'-Amidoquinoline. By ADOLPH CLAUS and WALTHER FROBENIUS (*J. pr. chem.*, 1897, **56**, 181—204. Compare Abstr., 1894, i, 617).—*4'-Amidoquinoline*, prepared by a method already described, melts at 70° after recrystallisation from the ordinary solvents; it contains $1H_2O$, which it loses at 100° , and then melts at 154° . It is easily soluble in alcohol, but less readily so in ether and benzene. The *hydrochloride* crystallises in small, colourless leaflets very readily soluble in water, and remains unchanged when heated to 300° ; the *platinochloride* forms orange-coloured needles containing $2H_2O$; the *nitrate* crystallises in small needles which melt at 214° after driving off $1H_2O$; and the *dichromate* crystallises in bunches of long, orange-red needles which decompose on exposure to air or on heating to 207° . On warming the base with methylic iodide at a temperature of 50 — 60° , it is completely transformed into the *methiodide*, which crystallises from alcohol in colourless needles melting at 224° ; the *methochloride*, prepared by treating the methiodide with silver chloride, crystallises in colourless needles melting at 310° ; the *metho-dichromate* crystallises in orange-red needles, becoming brown on exposure to air, and melting at 225° with decomposition, whilst the *ethiodide* crystallises in colourless needles melting at 232° .

When 4-amidoquinoline methiodide is treated with moist silver oxide or concentrated potash, small amounts of the ammonium hydroxide base are formed, and in their behaviour towards these reagents the quaternary 4'-amidoquinoline compounds take up a position intermediate between the para- and ortho-alkoxyquinoline derivatives. (Compare Claus and Howitz, Abstr., 1891, i, 1252.)

4'-Acetamidoquinoline, $NHAc \cdot C_9H_6N + H_2O$, crystallises from water in colourless, glistening needles, melts at 172° , and sublimes without decomposition. The *methiodide*, formed by heating the base with methylic iodide in sealed tubes at 120° , crystallises from alcohol in yellow leaflets, becoming black on heating to 250° , and melting at 291° with decomposition.

Claus and Howitz have already shown that when 4'-amidoquinoline is treated with sodium nitrite in hydrobromic acid solution, no diazo-derivative is obtained, but only 3'-bromo-4'-amidoquinoline, and also, as is now proved, 3'-bromoquinoline melting at 29 — 30° .

3'-Iodo-4'-amidoquinoline, prepared in a similar manner, crystallises from water in colourless needles containing $1H_2O$ and melting at 197° .

4'-Iodoquinoline is obtained in small quantities when 4'-amidoquinoline is diazotised in concentrated sulphuric acid solution and the product treated with potassium iodide. It is insoluble in cold water,

readily soluble in alcohol and ether, crystallises in colourless needles or prisms melting at 97° , and sublimes without decomposition. The *platinochloride* crystallises in orange-red needles, decomposing when heated to 185° with elimination of iodine; and the *methiodide* separates from water in bunches of reddish-yellow needles which decompose when heated to 251° .

By the action of nitric acid alone, 4'-amidoquinoline does not yield a nitro-compound, but the nitro-derivative of kynurine. *Nitro-4'-amidoquinoline* may, however, be produced by gradually adding 4'-amidoquinoline sulphate to well cooled fuming nitric acid; it crystallises from water in long, yellow needles containing $1\text{H}_2\text{O}$, and decomposes when heated to 207° . In all probability, the nitro-group is in the 3'-position of the pyridine ring, as the substance is easily dissolved by alkalis; the *sodium* compound forms small, colourless needles. It is very feebly basic, for although the *hydrochloride* may be obtained as colourless needles by adding the calculated amount of hydrochloric acid to an alcoholic solution of the base, it is immediately dissociated in presence of water. The *platinochloride* forms orange-red crystals, which decompose at 210° , and are at once dissociated in presence of water. The nitro-derivative is indifferent towards alkyl halogen compounds and does not form a diazo-compound.

Dinitro-4'-amidoquinoline, prepared by treating 4'-amidoquinoline with a mixture of nitric and sulphuric acids, crystallises from dilute alcohol in golden-yellow needles which decompose suddenly when heated to 203° . It does not form salts with acids, neither does it combine with methylic iodide, or give a diazo-compound. The *platinochloride* can be obtained with difficulty, but it dissociates immediately in presence of water.

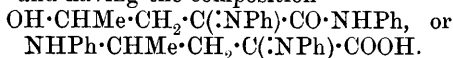
During the nitration, a second substance is formed in small amount crystallising from dilute alcohol, and decomposing at 285° . Its nature and composition will be further investigated, but it appears to be represented by one of the two formulæ $\text{C}_{18}\text{H}_{12}\text{N}_7\text{O}_7$ or $\text{C}_{18}\text{H}_{10}\text{N}_7\text{O}_7$.
A. W. C.

2'-Amidoquinoline. By ADOLPH CLAUS and S. SCHALLER (*J. pr. chem.*, 1897, 56, 204—212. Compare preceding abstract).—2'-*Amidoquinoline* is prepared by heating 2'-chloroquinoline, ammonium carbonate and ammonium hydroxide in sealed tubes for 5—6 hours at 200 — 210° , and is separated from the carbostyryl formed at the same time by treatment with benzene, in which the latter is insoluble. It crystallises from water in large, colourless or slightly yellow leaflets, melts at 125° , is readily soluble in ether, alcohol, and benzene, almost insoluble in chloroform and light petroleum, and sublimes readily in large, glistening, iridescent crystals; in contact with alkalis, it is converted into carbostyryl. The *platinochloride* forms glistening orange-yellow crystals containing $2\text{H}_2\text{O}$; the *methiodide* crystallises from alcohol in colourless needles and from water in prismatic crystals melting at 245° , and the *methochloride* forms silken needles melting at 265° .

The methiodide differs markedly from the corresponding derivative of 4'-amidoquinoline in giving with moist silver oxide a considerable

quantity of the quaternary ammonium hydroxide base. This subject will be treated more fully in a subsequent paper. A. W. C.

Action of Aromatic Amines on Certain Unsymmetrical Ketonic Compounds. By LOUIS SIMON (*Ann. Chim. Phys.*, 1896, [vii], 19, 433—536. Compare Abstr., 1893, i, 552; 1894, i, 509; 1895, i, 594, and 1896, i, 85).—Aniline reacts with pyruvic acid in the presence of ether, yielding three products, (1) anilpyruvic acid $\text{NPh}\cdot\text{CMe}\cdot\text{COOH}$, (2) 2'-methylquinoline-4'-carboxylic acid (aniluvitonic acid), and (3) a colourless, crystalline compound, $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$, melting at 190° and having the composition



Other primary aromatic bases react in the same manner.

With pyruvic acid, paratoluidine yields *paratolilpyruvic acid* melting at 127° , 3:2'-dimethylquinoline-4'-carboxylic acid melting at 265° , and the compound $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$, forming white crystals and melting at 238° ; orthotoluidine yields *orthotolilpyruvic acid* melting at 137° , 1:2'-dimethylquinoline-4'-carboxylic acid melting at 252° , and the compound $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$ melting at 232° ; whilst metaxylinidine yields *metaxylilpyruvic acid* melting at $137\text{--}138^\circ$, a trimethylquinoline-4'-carboxylic acid [$\text{Me}_3 = 1:3:2'$] melting at 212° , and the compound $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2$ melting at 232° .

β -Naphthylamine in like manner gives *β -naphthilpyruvic acid* melting at 132° , a compound melting at 232° , and as Doebner and others have already shown, *β -naphthyluvitonic acid*.

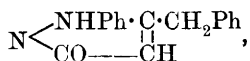
The compounds with aniline have already been prepared by Boettinger, who, however, ascribed somewhat different constitutions to them. The products formed from aniline and the ethereal salts of pyruvic acid have already been described (Abstr., 1896, i, 85). α -Naphthylamine does not react with pyruvic acid. J. J. S.

Ethylc Phenacetylmalonate. By HERMANN METZNER (*Annalen*, 1897, 298, 374—390. Compare Schott, Abstr., 1896, i, 700).—Ethylc phenacetylmalonate is converted into benzyl methyl ketone when heated with hydrochloric acid (sp. gr. = 1.1) for several hours; alcoholic potash resolves it into phenylacetic acid. Concentrated aqueous ammonia gives rise to phenylacetamide and malonamide, and aniline, which acts less rapidly, converts it into phenylacetanilide.

Ethylc benzylisoxazolonecarboxylate, $\text{O} \begin{array}{l} \text{N}=\text{C}\cdot\text{CH}_2\text{Ph} \\ \text{CO}\cdot\text{CH}\cdot\text{COOEt} \end{array}$, is prepared

by heating ethylc phenacetylmalonate dissolved in 60 per cent. alcohol with hydroxylamine hydrochloride and sodium carbonate on the water bath; it softens at 124° , and melts at 143° . The alcoholic solution gives a deep red coloration with ferric chloride, but does not reduce boiling Fehling's solution. The *silver* derivative is white, and the *aniline* compound melts and decomposes at 160° .

On heating ethylc phenacetylmalonate with phenylhydrazine, Schott obtained ethylc 1:5:3-phenylbenzylpyrazolone-4-carboxylate (*loc. cit.*); if, however, the salt is heated with a solution of the base in glacial acetic acid, 1:5:3-phenylbenzylpyrazolone,



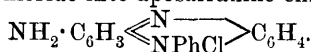
is produced, and crystallises in plates melting at 131—134°. It develops a deep red coloration with ferric chloride, but does not give Bülow's reaction for hydrazides.

Ethylic 1:3-dihydroxynaphthalene-2-carboxylate is obtained by dissolving ethylic phenacetylmalonate in concentrated sulphuric acid, and pouring the liquid into cold water; it crystallises from dilute alcohol or acetic acid in yellowish needles, and melts at 83—84°. The alcoholic solution gives a blue coloration with ferric chloride. The *diacetyl* derivative crystallises in slender, white needles, and melts at 64°. The *diamine*, which is produced in small quantity when the substance is heated with aqueous ammonia at 100°, melts at 168—172°, and its solution becomes coloured in consequence of oxidation. The *monanilide* derivative crystallises from acetic acid in rhombic plates, and melts at 185°. The *dibromo*-derivative crystallises in yellow needles, and melts at 159—160°; the alcoholic solution gives a blue coloration with ferric chloride.

1:3-Dihydroxynaphthalene-2-carboxylic acid is prepared from the ethylic salt by heating it with aqueous baryta at 80°, hydrogen being passed through the solution during the operation; it crystallises from water in clusters of yellowish needles, and melts at 145°, when it evolves carbonic anhydride. The *silver* salt has been analysed. When the acid is boiled with water, it is converted into 1:3-dihydroxynaphthalene (Friedländer and Rüdtt, Abstr., 1896, i, 569).

M. O. F.

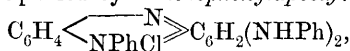
Salts of Phenylphenazonium and Phenyl-naphthophenazonium and their Reaction with Alkalis and Amines. By FRIEDRICH KEHRMANN and W. SCHAPOSCHNIKOFF (*Ber.*, 1897, 2620—2628. Compare Abstr., 1897, i, 172).—*Phenylphenazonium dichromate*, $(\text{C}_{18}\text{H}_{13}\text{N}_2)_2\text{Cr}_2\text{O}_7$, forms small, ochre-yellow prisms; the *platinochloride* is a sparingly soluble, brownish-yellow, crystalline powder, and the *aurochloride* a heavy, ochre-yellow precipitate; the *chloride* has only been obtained in solution; the *iodide* is a brown, crystalline precipitate, and the *mercurochloride* and *picrate* are also crystalline precipitates. Phenylphenazonium ferric chloride is converted by aqueous soda into aposafranone, $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}$, identical with the product obtained by Jaubert (Abstr., 1895, i, 219). Alcoholic ammonia converts phenylphenazonium ferric chloride into aposafranine chloride,



The hydro-derivative of the phenazonium compound, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \text{---} \\ \text{NPh} \end{array} \text{C}_6\text{H}_4$, is also formed, but is rapidly oxidised by the oxygen of the air, and is thus reconverted into the original phenazonium derivative, which then again reacts with the ammonia, all the original substance being finally converted into aposafranine, or decomposed by secondary reactions.

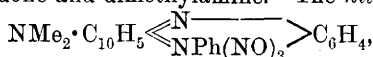
Dimethylaposafranine nitrate, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPh(NO}_3) \end{array} \text{C}_6\text{H}_4$, obtained by acting on the phenylphenazonium ferric chloride with

dimethylamine and precipitating with sodium nitrate, crystallises with $\frac{1}{2}\text{H}_2\text{O}$ in thick prisms with a bronze lustre. The *platinochloride* forms lustrous granules, and the *dichromate* a brownish-violet, crystalline powder. The salts give bluish-green solutions in sulphuric acid, which become violet on the addition of water. Aniline converts the phenylphenazonium ferric chloride into the phenylposafrafranine chloride previously obtained by Fischer and Hepp (Abstr., 1897, i, 636). This is accompanied by *anilidophenylaposafranine chloride*,



which crystallises in granules with a green, metallic lustre. The salts of phenyl-naphthophenazonium are converted by concentrated soda into rosindone, $\text{O} \begin{array}{c} \text{C}_{10}\text{H}_5 \cdot \text{N} \\ \text{NPh} - \text{C}_6\text{H}_4 \end{array}$, and by ammonia into rosinduline chloride,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \text{NPhCl} \end{array} \text{C}_{10}\text{H}_5 \cdot \text{NH}_2$. Dimethylamine produces salts of dimethylrosinduline, which readily decompose in alkaline solution with formation of rosindone and dimethylamine. The *nitrate*,

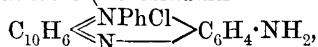


crystallises with $\frac{1}{2}\text{H}_2\text{O}$ in prisms with a greenish lustre. The *platinochloride* and *dichromate* are sparingly soluble, crystalline precipitates.

A. H.

Salts of Phenylisonaphthophenazonium and the Action of Amines on them. By FREDERICH KEHRMANN and WILHELM HELWIG (*Ber.*, 1897, 30, 2629—2636. Compare Abstr., 1897, i, 107, 172).—

Phenylisonaphthophenazonium hydroxide, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{NPh(OH)} \end{array} \text{C}_6\text{H}_4$, is formed, together with a small amount of phenyl-naphthophenazonium hydroxide, by the condensation of β -naphthaquinone with amidodiphenylamine. Some of its salts have already been described. The double ferric chloride crystallises in lustrous, orange-yellow plates melting at 200.5° ; the *nitrate* forms reddish-yellow, compact crystals, which melt and decompose at 229° ; the *platinochloride* is an orange-red, crystalline powder; the *aurochloride* melts at 240° , and the *dichromate* is a scarlet-red powder. The salts of phenylisonaphthophenazonium are converted into amido-derivatives by alcoholic ammonia. 3-*Amidophenylisonaphthophenazonium chloride* (isorosinduline chloride, No. 4),

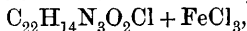


crystallises in violet-red needles which dissolve in water, forming a magenta-red solution, from which aqueous soda precipitates the free base; the *platinochloride* crystallises in violet needles, and the *nitrate* in flat prisms with a coppery lustre. 3-*Dimethylamidophenylisonaphthophenazonium nitrate* (dimethylisorosinduline nitrate), $\text{C}_{24}\text{H}_{20}\text{N}_3 \cdot \text{NO}_3$, is obtained by the action of dimethylamine on the isonaphthophenazonium salts. It crystallises in indigo-blue prisms with a coppery lustre, and melts with decomposition at 220° . The *aurochloride* forms blue crystals which melt and decompose at 200 — 203° ; the *platinochloride* also forms blue crystals. 3-*Phenylamidophenylisonaphthophenazonium*

chloride (phenylisorosinduline chloride), prepared by heating the double ferric chloride with aniline, is a heavy, crystalline powder almost insoluble in cold water; its *platinochloride* is an insoluble, blue, crystalline precipitate.

The position of the amido-group in these derivatives has not been definitely ascertained, but from the analogy of the phenylnaphthophenazonium compounds it is probable that it takes up the para-position relatively to the azine nitrogen atom. A. H.

The Fifth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and O. FEDER (*Ber.*, 1897, 30, 2637—2641).—*Nitrorosinduline chloride*, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_5 \cdot \text{N} \begin{smallmatrix} \text{---} \text{N} \text{---} \\ \text{---} \text{N} \text{PhCl} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NO}_2$, obtained by heating nitramidodiphenylamine hydrochloride with oxynaphthaquinonimide in alcoholic solution (Rademacher, These, Berlin), is a heavy, dark red, crystalline powder with a greenish lustre. A number of derivatives of this compound have been prepared and will be described by Rademacher in another communication. When this substance, in acid solution, is treated with sodium nitrite, and then with alcohol, hydrogen is substituted for the amido-group, and salts of 4-nitrophenylnaphthophenazonium are formed. The *double ferric chloride*,

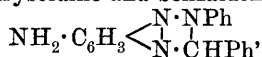


is a reddish-brown, sandy, crystalline powder. The *nitrate* forms green, metallic looking-needles. The aqueous solutions of both this and the other salts decomposes when warmed, nitrorosindone being deposited. The *chloride* crystallises with $2\text{H}_2\text{O}$ in green needles; the *platinochloride*, *aurochloride*, and *dichromate* are insoluble crystalline precipitates.

The nitro-compound can readily be converted by reduction into the corresponding amido-derivative, *isorosinduline chloride* (No. 5), $\text{C}_{10}\text{H}_6 \cdot \text{N} \begin{smallmatrix} \text{---} \text{N} \text{---} \\ \text{---} \text{N} \text{PhCl} \end{smallmatrix} \text{C}_6\text{H}_5 \cdot \text{NH}_2$, which crystallises in long, lustrous, black-violet needles, and is readily soluble in water; the *nitrate* crystallises with $1\text{H}_2\text{O}$, and is almost insoluble in dilute nitric acid; the *platinochloride* forms bluish-black, insoluble needles. A. H.

Triazine Derivatives from Chrysoidine and from Orthamidoazotoluene. By EMILIO NOELTING and F. WEGELIN (*Ber.*, 1897, 30, 2595—2604).—Diamidoazo-compounds react with benzaldehyde in a similar manner to monamido-compounds (Goldschmidt and Rosell, *Abstr.*, 1890, 614), triazine derivatives being formed, which are capable of undergoing the diazo-reaction.

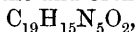
The *triazine* from chrysoidine and benzaldehyde,



is a yellowish powder, solutions of which rapidly become brown in the air. The *sulphate* is sparingly soluble. The *acetyl* derivative is a white powder which melts at 216° ; the *benzoyl* derivative melts at 221° . The triazine readily forms diazo-salts, which yield red colouring matters with β -naphthol, resorcinol, and other phenols and amido-compounds. Fuming sulphuric acid converts the triazine into a mixture of

sulphonic acids, which have an extremely sweet taste. The sulphotriazines obtained from sulphonated chrysoidines all have this sweet taste, whereas the compound from chrysoidine and benzaldehydemeta-sulphonic acid has a bitter taste. When the amido-group of chrysoidine-parasulphonic acid is replaced by hydrogen, the salts of the resulting acid, which crystallises in needles, also have a sweet taste. These three acids are all insoluble in cold water, sparingly soluble in hot water.

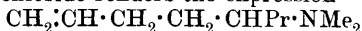
The *triazine* from chrysoidine and orthonitrobenzaldehyde,



crystallise in yellow tablets, melts and decomposes at 118—119°, and on reduction yields an *amido*-compound, which melts and decomposes at 204°. The *triazine* from metanitrobenzaldehyde forms yellow crystals which melt and decompose at 204—205°. The *amido*-compound melts and decomposes at 187°. The *triazine* from paranitrobenzaldehyde forms red crystals which melt and decompose at 211°, and are less soluble than those of the ortho-compound. The *amido*-derivative melts at 200°. The colouring matters formed from the azo-derivatives of these three amidotriazines with amidonaphtholsulphonic acid $\text{G}, [\text{NH}_2 : \text{OH} : \text{SO}_3\text{H} = 1 : 1' : 3']$, and amidonaphtholdisulphonic acid $\text{H}_2, [\text{NH}_2 : \text{OH} : (\text{SO}_3\text{H})_2 = 1 : 1' : 3 : 3']$ have also been examined. They dye cotton without mordants violet to blue, but are not fast to acids. The ortho-compounds have the least colouring power, the para-compounds the greatest.

The *triazine* from orthamidoazotoluene and orthonitrobenzaldehyde, $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_2$, crystallises in yellow needles melting at 230°. The *triazine* from the metanitrobenzaldehyde forms yellowish needles melting at 228°, whilst that from the para-compound melts at 264°. Metahydroxybenzaldehyde yields a *triazine*, $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$, which crystallises in white needles melting at 265°. Metasulphobenzaldehyde yields a *triazine*, $\text{C}_{21}\text{H}_{19}\text{N}_3\text{SO}_3$, which is a crystalline powder. Phthalic anhydride does not yield analogous compounds with amidoazotoluene, but simply forms an acid derivative. A. H.

Dimethylconiine. By MARTIN MUGDAN (*Annalen*, 1897, 298, 131—147. Compare Abstr., 1894, i, 555).—It has been pointed out (*loc. cit.*) that whilst the optical activity of dimethylconiine appears to condemn the formula $\text{CHPr} \cdot \text{CH} \cdot [\text{CH}_2]_3 \cdot \text{NMe}_2$, its abnormal behaviour towards hydrogen chloride renders the expression



equally improbable; the constitution of the base has been therefore expressed by the formula $\text{NMe}_2 \cdot \text{CH} < \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{CHPr} \cdot \text{CH}_2 \end{array}$. The author, how-

ever, finds that dimethylpentamethenylamine, $\text{NMe}_2 \cdot \text{CH} < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, which should resemble in behaviour the higher homologues, dimethyl- α -pipercoline and dimethylconiine, differs from them greatly. Dimethylconiine, moreover, obtained by distilling dimethylconium hydroxide, can be resolved into three fractions which exhibit marked differences in optical activity, and from a study of the behaviour of crude dimethylconiine towards hydrogen iodide, it appears that

methylconiine is present in the base. In addition to this substance, the crude base consists of two isomeric dimethylconiines, yielding the two corresponding dihydrodimethylconiines on reduction; one of these products has been identified as normal dimethyloctylamine.

It is shown, therefore, that when dimethylconium hydroxide is submitted to distillation, change proceeds in three directions. In the first place, methylic alcohol is eliminated, giving rise to a small quantity of methylconiine; when, however, water is separated, scission occurs between nitrogen and the 2-carbon atom on the one hand, giving rise to dimethylconiine of the formula $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPr}\cdot\text{NMe}_2$, whilst on the other hand the base of the formula $\text{CHPr}\cdot\text{CH}\cdot[\text{CH}_2]_3\cdot\text{NMe}_2$ is produced when scission occurs between nitrogen and the 6-carbon atom.

Dimethylpentamethenylamine, $\text{NMe}_2\cdot\text{CH}\left\langle\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{array}\right\rangle$, is prepared from pentamethenylamine by the action of methylic iodide, and conversion of the substituted ammonium iodide into the ammonium chloride, which is then distilled at 330° ; it is a colourless base having the odour of trimethylamine, and boils at $133\cdot5\text{--}135^\circ$. Unlike pentamethenylamine, it is scarcely soluble in water; the *hydrochloride* crystallises from acetone in colourless, hygroscopic leaflets. Both the original base and the dimethyl derivative are coloured by one drop of an alcoholic solution of iodine, whilst the latter is immediately decolorised by dimethylconiine. Dry dimethylpentamethenylamine hydrochloride absorbs hydrogen chloride, which causes it to liquefy, but the halogen is completely removed by water, which is not the case with hydrochloro-dimethylconiinehydrochloride. The aurochlorides of dimethylpiperidine, dimethylpipercoline, and dimethylconiine, moreover, differ from the aurochloride of dimethylpentamethenylamine in their unstable character, the solution of the last-named salt undergoing no change when boiled.

When dry hydrogen iodide is passed into dimethylconiine, it is found that, in addition to methylconiine, the base consists of a mixture of two isomerides; the *hydriodide* of one crystallises in short prisms and melts at 220° , whilst the *hydriodide* of the other, which is produced in four times the amount, is more readily soluble in a mixture of alcohol and ethylic acetate, from which it crystallises in thick needles and melts at $151\text{--}152^\circ$. A 10 per cent. solution of the former salt has $\alpha = 5\cdot2^\circ$, whilst the hydriodide of lower melting point has $\alpha = 0\cdot36^\circ$. The derivatives of the latter salt closely resemble those of dimethylconium iodide, and the chloride on distillation yields a base which boils at $173\cdot5\text{--}177^\circ$, and has the odour and formula of methylconiine.

Dimethyldihydroconiine, $\text{C}_{10}\text{H}_{23}\text{N}$, obtained by reducing the product of the action of hydrogen iodide on dimethylconiine, with zinc dust and glacial acetic acid, has the odour of the base from which it is derived; it boils at $184\text{--}186^\circ$, has the sp. gr. = $0\cdot7795$ at $14^\circ/4^\circ$, the refractive index $n_D = 1\cdot4288$, and the rotation angle $\alpha = 3\cdot6^\circ$ in a 1 decimetre tube. The *aurochloride* crystallises in elongated leaflets, and is stable in solution; the *platinochloride* melts at 117° . Methylic iodide gives rise to a mixture which melts at 166° , and consists of the

methiodide which melts at 139—141°, and the somewhat more readily soluble *methiodide* melting at 190°; the former of these has been identified with trimethyloctylammonium iodide which melts at 139—141°, whilst the *platinochloride* and *aurochloride* melt at 240°, and 91—93° respectively. M. O. F.

Derivatives of Theobromine. Action of Chloroform on Phenylhydrazine. By HEINRICH BRUNNER and HEINRICH LEINS (*Ber.*, 1897, 30, 2584—2587).—The *propyl*, *isopropyl*, *butyl*, and *amyl* derivatives of theobromine were obtained by heating silver theobromine with the corresponding iodide. All these substances form crystalline granules melting above 270°.

Van der Slooten (*Abstr.*, 1897, i, 382) has prepared a series of alkyltheobromines by the action of alkyl iodides on an alcoholic solution of potassium theobromine, and in this way has obtained compounds of comparatively low melting point, which differ from those just described. *Nitro-theobromine* $\text{NO}_2 \cdot \text{C}_7\text{H}_7\text{N}_4\text{O}_2$, obtained by the direct action of nitric acid on theobromine, forms a pale yellow, micro-crystalline powder, which can be sublimed. The corresponding *amido*-compound is sparingly soluble in alcohol and can also be sublimed.

When chloroform is heated or allowed to stand with phenylhydrazine, the hydrochloride of the latter is produced. No carbophenylhydrazine appears to be formed. A. H.

New Decomposition of Theobromine. By EMIL FISCHER and FRITZ FRANK (*Ber.*, 1897, 30, 2604—2618).—When theobromine is suspended in chloroform and treated with chlorine, it is converted into an unstable substance rich in chlorine which separates in crystals but decomposes even in dry air. Its composition has not been ascertained. When this substance is treated with water it yields

theobromuric acid, $\text{COOH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NMe} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \text{N} - \text{CO} \end{smallmatrix}$, which crystal-

lises from lukewarm water in small, colourless needles or prisms, melts with evolution of gas at about 181° (corr.), and does not reduce ammoniacal silver oxide or give the murexide reaction. It readily undergoes etherification, yielding ethereal salts, which are also formed by the action of alcohols on the chlorine derivative; the *ethylic* salt forms compact, colourless prisms terminated by pyramids, and melts at 212° (corr.); the *methylic* salt also crystallises well and melts at 199—200° (corr.). Hot water decomposes theobromuric acid with evolution of carbonic anhydride and formation of the *methylcarbamide salt of methylparabanic acid*; this melts at 127—128° (corr.), decomposes at about 195°, and is converted by alkalis into methylcarbamide and oxalic acid, whilst hydrochloric acid decomposes it with formation of the carbamide and methylparabanic acid. It can readily be obtained by the union of its constituents, and is also formed when methylcarbamide is heated with ethylic oxalate at 100°; this reaction affords a new synthesis of methylparabanic acid. The constitution of theobromuric acid has not been definitely ascertained.

Hydriodic acid converts both the free acid and its ethereal salts into

the *anhydride of hydrotheobromuric acid*, $C_7H_8N_4O_4$, which crystallises in long, colourless needles and melts and decomposes at 264° (corr.); it dissolves in alkalis, forming salts of *hydrotheobromuric acid*, $C_7H_{10}N_4O_5$, which separates when these solutions are acidified, and crystallises with $1H_2O$ in long, colourless, matted needles. The acid becomes anhydrous at 110° and then melts and decomposes at 231° (corr.). It is reconverted by 20 per cent. hydrochloric acid into the anhydride. The *ethylic salt* crystallises in matted needles melting at $206-207^\circ$ (corr.). Dilute baryta water converts hydrotheobromuric acid into carbonic anhydride, methylamine, and *theuric acid*, $C_5H_7N_3O_4$; the latter is readily soluble in hot water, crystallises in rhombic prisms, melts and decomposes at about 254° (corr.). It reduces ammoniacal silver oxide and is decomposed by excess of alkali; the constitution of the acid has not been ascertained.

When ethylic theobromurate is dissolved in concentrated hydrochloric acid, a compound is formed which dissolves in water, with evolution of gas and formation of *carbonyldimethylcarbamide*, $CO(NH \cdot CO \cdot NHMe)_2$. This substance, which can be obtained by the action of phosgene on dimethylcarbamide, is a granular, crystalline powder melting at $199-200^\circ$ (corr.). It is not precipitated from a warm aqueous solution by mercuric nitrate, and gives no coloration with copper sulphate in alkaline solution; these two reactions distinguish it from carbonyldicarbamide. It dissolves without change in cold dilute aqueous alkalis, but on boiling is decomposed with formation of methylcyanuric acid.

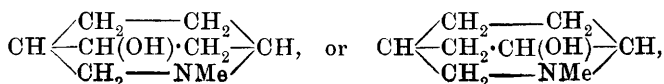
Nitrous acid converts it into *nitrosocarbonyldimethylcarbamide*, $C_5H_9N_4O_3 \cdot NO$, which is a yellow, flocculent precipitate that cannot be recrystallised, and is decomposed by hot water with formation of methylcyanuric acid and methylbiuret. *Methylcyanuric acid*, $C_4H_5N_3O_3$, crystallises with $1H_2O$ in thin plates, and when dry melts at $296-297^\circ$ (corr.); it sublimes readily and can be distilled in small quantities, yielding a very penetrating vapour. When treated with aqueous potash and methylic iodide, it is converted into trimethylic isocyanurate. *Methylbiuret*, $C_3H_7N_3O_2$, crystallises in prisms, melts at $165-166^\circ$ (corr.) and yields a reddish-violet coloration with a dilute alkaline solution of copper sulphate. The *nitroso-derivative* is an almost colourless powder, which melts and decomposes at about 135° .

A. H.

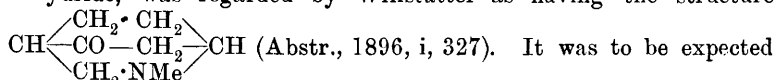
Ketones of the Tropine Group. VIII. Constitution of Tropine.

By RICHARD WILLSTÄTTER (*Ber.*, 1897, 30, 2679—2719. Compare *Abstr.*, 1897, i, 304, and 1896, i, 655, 707).—The fact that condensation of tropinone with benzaldehyde gives rise to a dibenzylidene derivative (*Abstr.*, 1897, i, 304), has led the author to reconsider the evidence which supports Merling's formula for tropine, with the result that it now appears necessary to submit this expression to very considerable modification.

In 1891, Merling first represented the constitution of tropine by the formula



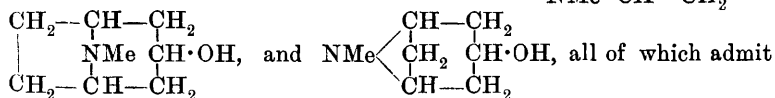
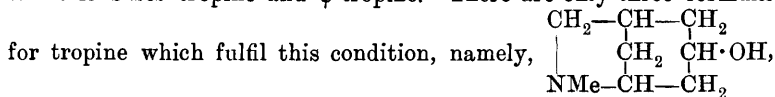
the position of the hydroxylic group being uncertain; accordingly, tropinone, the ketone obtained by oxidising tropine with chromic anhydride, was regarded by Willstätter as having the structure



from the behaviour of camphor and menthone towards benzaldehyde in presence of hydrogen chloride, that tropinone would yield a benzylidene derivative analogous to benzylidenecamphor and benzylidenementhone; as already stated, however, the product is dibenzylidenetropinone, and this circumstance is regarded by the author as indicating the presence of the group $-\text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2-$ in the ketone.

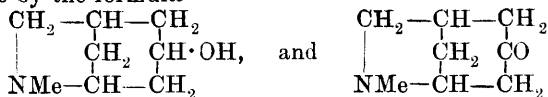
In addition to the behaviour of tropinone towards aldehydes, support is lent to this view by the action of ethylic oxalate, amylic nitrite, and diazobenzene chloride. It is known that the introduction of acidic radicles into ketones by means of sodium ethoxide affords a method of determining the number of methylenic groups in immediate connection with carbonyl, acetone, for instance, first yielding ethylic acetone-oxalate, $\text{COMe} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{COOEt}$, and then ethylic xanthochelidonate, $\text{CO}(\text{CH}_2 \cdot \text{CO} \cdot \text{COOEt})_2$; similarly, tropinone is converted by ethylic oxalate and sodium ethoxide, first into ethylic tropinoneoxalate, $\text{C}_8\text{H}_{12}\text{NO} \cdot \text{CO} \cdot \text{COOEt}$, and subsequently into ethylic tropinonedioxalate, $\text{C}_8\text{H}_{11}\text{NO}(\text{CO} \cdot \text{COOEt})_2$. Again, when amylic nitrite acts on tropinone under the influence of hydrogen chloride dissolved in glacial acetic acid, di-isonitrosotropinone, $\text{C}_8\text{H}_{11}\text{N}_3\text{O}_3$, is produced, affording strong evidence of the presence of two methylenic groups attached to carbonyl; the compound produced in this manner may be regarded as the 1:3-dioxime of *tropanetrione*, the 1:2:3-triketone of the tropine series. Furthermore, diazobenzene in acetic acid solution converts tropinone into the compound $\text{C}_{20}\text{H}_{21}\text{N}_5\text{O}$, which constitutes the 1:3-diphenylhydrazone of *tropanetrione*.

In the author's estimation, these observations establish the existence of the group, $:\text{C} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}:$, in tropinone, the corresponding alcohol complex, $:\text{C} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}:$, being present in the two isomeric bases tropine and ψ -tropine. There are only three formulæ



of the presence of the complex, $:\text{C} \cdot \text{NMe} \cdot \text{CH}(\text{CH}_2\text{R})$, in tropidine. The third expression is excluded, however, because it does not account for the production of dihydrobenzaldehyde from tropinone methiodide and sodium carbonate (Willstätter, Abstr., 1896, i, 327); nor does it agree with the formation of normal adipic acid on oxidation of tropilene (Ciamician and Silber, Abstr., 1896, i, 397), and by treatment of methylic tropinate methiodide with potash (Willstätter, Abstr., 1896, i, 266). The latter consideration leads the author to abandon also the second of the above formulæ, and he therefore expresses tropine and

tropinone by the formulæ

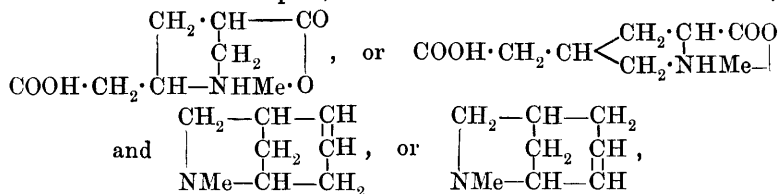


respectively.

According to this view, *tropan*, the name by which the author

distinguishes hydrotropidine, $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ | \quad | \quad | \\ \text{NMe} - \text{CH} - \text{CH}_2 \end{array}$, is a cyclic combina-

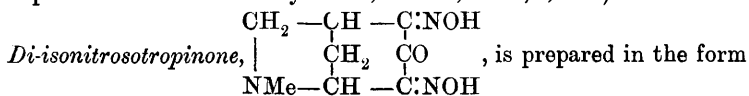
tion of *n*-methylpyrrolidine with hexahydrobenzene, the periphery of the ring being composed of 6 carbon atoms and 1 atom of nitrogen; and as the two constituent members of the combination have 3 carbon atoms in common, tropine must be looked on as a hexahydrophenol in which the meta-substituents are linked. From this conception of the structure of tropine, there follow the alternative formulæ,



for tropinic acid and tropidine respectively, the former in each case being the one which the author regards as the more probable.

Tropinic acid and tropidine being, as it were, the points of contact of the atropine and cocaine groups, it follows that ecgonine and anhydroecgonine are likewise derivatives of tropan, and the formulæ for these substances put forward by Einhorn and Tahara (Abstr., 1893, i, 377) will therefore require modification in this direction.

The modified view of the structure of tropine emphasises the analogy between the bases of this series and those derived from the rind of pomegranate root. It also becomes clear that the *n*-methylpyrrolidine ring is common to all the alkaloids of the atropine and cocaine groups (compare Liebermann and Cybulski, Abstr., 1895, i, 310).



of hydrochloride by dissolving tropinone (20 grams) in amylic nitrite (40 grams), and treating the cooled solution with glacial acetic acid (120 grams) previously saturated with hydrogen chloride at 0°; the hydrochloride which separates is washed with acetic acid and with alcohol, and treated in aqueous solution with sodium acetate, or with caustic soda followed by acetic acid. Di-isonitrosotropinone crystallises from water in bright yellow, transparent prisms, and decomposes with slight explosion at 197°; it is both basic and acidic, the aqueous solution reddening litmus. It does not give Liebermann's reaction, and develops a reddish-brown coloration with ferric chloride, whilst ferrous sulphate colours the aqueous solution an intense green; alkaline and acid solutions of potassium permanganate are immediately decolorised by

the substance, which does not, however, reduce Fehling's solution. Alkali hypochlorites readily oxidise the nitroso-compound, the yellow colour of the solution in alkalis being completely destroyed; oxidation with nitric acid gives rise to a pyrroline derivative. The *hydrochloride*, prepared in the manner described, crystallises from water in lustrous, rhombohedral plates; it becomes brown at 200° and decomposes with explosion at 260°. The *hydrobromide*, which crystallises from water in bright yellow, lustrous prisms, becomes brown at 200° and explodes at 253°. The *mono-silver* derivative forms minute needles, is insoluble in water, resists the action of light, and explodes when heated; the *silver* derivative is dark-brown and crystalline. The *dibenzoyl* derivative crystallises from dilute acetic acid in slender, long needles, and melts and decomposes at 172°; when boiled with caustic soda, it yields ammonia, hydrogen cyanide, and pyrroline bases, and it is also decomposed by boiling glacial acetic acid.

The *anhydride* of di-isonitrosotropinoneoxime (tri-isonitrosotropan), $\text{C}_5\text{H}_9\text{N}-\text{C}:\text{N} > \text{C}(\text{NOH})\cdot\text{C}:\text{N} > \text{O}$, is obtained by heating a solution of di-isonitrosotropinone in alkali with excess of an alkaline solution of hydroxylamine, and then acidifying with glacial acetic acid; the furazan crystallises from alcohol in long, silky needles, and explodes at 185–186°. The aqueous solution gives a brown coloration with ferric chloride. The *hydrochloride* crystallises from water in six-sided plates, and decomposes vigorously at about 220°; the *benzoyl* derivative crystallises from alcohol in small, lustrous needles, and melts at 150–152°.

The action of phenylhydrazine on di-isonitrosotropinone is somewhat complicated, and gives rise to two substances. The *compound* $\text{C}_{23}\text{H}_{36}\text{N}_{10}\text{O}_5$, obtained from the free nitroso-compound, crystallises in reddish-yellow, six-sided plates, and melts at 177–178°; the *compound*, $\text{C}_{28}\text{H}_{33}\text{N}_9\text{O}_4$ arises from di-isonitrosotropinone hydrochloride, and crystallises in orange-red leaflets which melt and decompose at 224–225°.

Tribromacetoxytropinone, $\text{C}_8\text{H}_9\text{NOBr}_3\cdot\text{OAc}$, is prepared by digesting a solution of tetrabromotropinone (Abstr., 1896, i, 709) in warm glacial acetic acid with silver acetate, the liquid being filtered after an interval and diluted with water; it crystallises from alcohol in short, highly refractive prisms, if deposited slowly in quadratic plates, and melts at 148°.

Tropantrione *diphenylhydrazone*, $\text{C}_{20}\text{H}_{21}\text{N}_5\text{O}$, is prepared by adding diazobenzene chloride to a solution of tropinone in dilute acetic acid and maintaining the temperature of the liquid at 0° during 3 hours; the acetate separates when the solution is allowed to evaporate spontaneously, and on decomposing this salt with caustic soda the diphenylhydrazone is obtained. It crystallises from absolute alcohol in rosette-like aggregates of dark-red, microscopic needles, and melts and decomposes at 130°; it separates in long, slender needles containing chloroform of crystallisation when the acetate is boiled with a mixture of chloroform and absolute alcohol. The diphenylhydrazone is a colouring matter, dyeing wool an orange-red; the solution in concentrated sulphuric acid is bluish-violet and in hydrochloric acid reddish-

violet, both liquids becoming red on dilution with water (compare von Pechmann and Jenisch, *Abstr.*, 1892, 161).

Ethylic tropinoneoxalate, $C_6H_{11}N \begin{smallmatrix} < CH \cdot CO \cdot COOEt \\ CO \end{smallmatrix}$, prepared from

tropinone and ethylic oxalate (1 mol.) under the influence of sodium ethoxide (2 mols.), crystallises from absolute alcohol in colourless, highly refractive, six-sided plates and melts at 169.5° , when it decomposes; the aqueous solution gives a deep cherry-red coloration with ferric chloride, and when boiled with acetic acid and sodium acetate yields a brown solution. The *platinochloride* forms red, microscopic leaflets containing $3H_2O$, and melts and decomposes at $194-195^\circ$; it is scarcely soluble in cold water, and is decomposed by the boiling liquid, giving rise to tropincne platinochloride. The *hydrochloride* of tropinoneoxalic acid is produced on boiling the ethylic salt with concentrated hydrochloric acid, and crystallises from alcohol in stellate aggregates of lustrous prisms; it melts and decomposes at 194° , and gives a deep cherry red coloration with ferric chloride.

Isonitrosotropinoneoxalic acid, $C_5H_9N \begin{smallmatrix} - CH \cdot CO \cdot COOH \\ C(NO) \cdot CO \end{smallmatrix}$, is obtained

by dissolving ethylic tropinoneoxalate with amylic nitrite (1 mol.) in glacial acetic acid, and treating the solution with glacial acetic acid saturated at 0° with hydrogen chloride; the product separates in bright yellow needles and prisms, but is very unstable. Ferric chloride develops a brown coloration, and the solution in alkalis is intense yellow.

Ethylic tropinonedioxalate, $C_8H_{11}NO(CO \cdot COOEt)_2$, is prepared by dissolving ethylic tropinoneoxalate in ethylic oxalate (2 mols.), and adding sodium ethoxide (2 mols.), free from alcohol, to the solution; after some hours, the liquid is treated with water, agitated with ether, and the aqueous portion removed and acidified with acetic acid. The salt crystallises from alcohol in yellow, transparent prisms, separating from methylic alcohol in yellow, pleochromatic plates; it melts and decomposes at 176° .

Difurfurylidenetropinone, $C_8H_{11}NO(C_5H_4O)_2$, is prepared by cautiously adding a solution of tropinone (1 mol.) and furfuraldehyde (2 mols.) in ether to the same medium containing sodium ethoxide (2 mols.) in suspension; it crystallises from absolute alcohol in canary-yellow prisms, and melts at 138° . The solution in concentrated sulphuric acid is of an intense violet-red, becoming yellow on dilution with water, which precipitates the *sulphate* in slender, lustrous needles; it decolorises bromine and an acid solution of potassium permanganate. It differs from dibenzylidenetropinone in its property of dyeing wool greenish-yellow. The *hydrochloride*, which crystallises in aggregates of microscopic prisms, melts and decomposes at $237-238^\circ$; the *methiodide* crystallises from water in yellow, pleochromatic plates, and melts at 281° , when it decomposes.

Although dibenzylidenetropinone was prepared in the first instance from tropinone and benzaldehyde under the influence of hydrochloric acid, caustic soda may be also employed as the condensing agent. If, however, sodium ethoxide is used, the dibenzylidenetropinone is obtained

mixed with the compound $C_{22}H_{23}NO_2$, arising from condensation of tropinone with benzaldehyde (2 mols.) involving the elimination of only $1H_2O$; it contains $\frac{1}{2}H_2O$, which is removed at 70° , and it melts and decomposes at 115° . The solution in concentrated hydrochloric acid is deep red, and remains cherry-red on dilution. The *methiodide* crystallises from alcohol in prisms, and melts at $186-187^\circ$, when it decomposes.

M. O. F.

Harmine and Harmaline. By OTTO FISCHER (*Ber.*, 1897, 28, 2481—2489. Compare Abstr., 1885, 821, and 1889, 730).—Harmaline has been shown to be dihydroharmine; both it and harmine are optically inactive in acetic acid solution. The oxidation of harmaline, $C_{13}H_{14}N_2O$, to harmine, $C_{13}H_{12}N_2O$, is best effected with potassium permanganate in dilute sulphuric acid solution. Methylharmine melts at 209° ; its *hydrochloride* and flesh-coloured *platinochloride*, $(C_{13}H_{11}MeN_2O)_2 \cdot H_2PtCl_6 + 2H_2O$, were prepared; it unites with more methylic iodide, yielding a quaternary *iodide*, $C_{13}H_{11}MeN_2O \cdot MeI$, which reacts with silver nitrate, forming the crystalline *nitrate*; the *platinochloride* and *aurochloride* of this quaternary base were also prepared. *Acetylharmaline*, $C_{13}H_{13}AcN_2O$, can be prepared by dissolving harmaline and fused sodium acetate in acetic anhydride, heating cautiously to 60° , and then setting it aside; it melts at $204-205^\circ$. *Methylharmaline*, prepared from harmaline methiodide by boiling it with baryta water, melts and decomposes at 162° , and will unite with more methylic iodide. Dihydroharmaline is best prepared by reducing harmaline with sodium in boiling amyl-alcoholic solution; its *acetyl* and *benzoyl* derivatives, $C_{13}H_{15}AcN_2O$, &c., melt at 239° and $158-159^\circ$ respectively. Harmine and harmaline are oxidised to harminic acid, $C_{10}H_8N_2O_4$, by chromic acid in boiling acetic acid solution, or by nitric acid, the same product being obtained when harmol, dichloroharmine, or nitroharmine is oxidised. This acid reacts with normal alkali like a monobasic acid, but with resorcinol, like a dibasic acid, forming a fluorescein. It reacts with methylic iodide and aqueous potash, yielding *methylharminic acid*, $C_{10}H_7MeN_2O_4$, which can also be obtained by the oxidation of methylharmine, and which blackens between 260° and 280° when heated; with ethylic iodide, it yields *ethylharminic acid*, $C_{10}H_7EtN_2O_4$, which blackens at 280° . Apoharmine, formed from harminic acid by the loss of 2 mols. of carbonic anhydride, yields a yellow *picrate* melting at 247° ; boiling concentrated nitric acid converts it into a derivative, $C_8H_7(NO_2)N_2$, which melts and decomposes at 270° , and is soluble in alkalis; with methylic iodide, it yields the hydriodide of *methylapoharmine*, $C_8H_7MeN_2$, which base melts at $77-78^\circ$, and yields a yellow *platinochloride* which decomposes at 260° .

C. F. B.

Organic Chemistry.

The Number of Isomeric Paraffins. By SIMA M. LOSANITSCH (*Ber.*, 1897, 30, 3059—3060. Compare this vol., i, 1).—A reply to Hermann (this vol., i, 101). The author is still of opinion that the number of possible isomeric hydrocarbons, $C_{12}H_{26}$, is 354, and not 355.
J. J. S.

Decomposition of Hydrocarbons of High Molecular Weight at a Moderate Temperature. By CARL ENGLER (*Ber.*, 1897, 30, 2908—2920).—The residues from the distillation of petroleum consist of unsaturated compounds, chiefly olefines and the products of their polymerisation. The oils which boil above 200° decompose when heated either in an open vessel or under pressure, the lower members of the paraffin series, together with olefines, naphthenes, and aromatic hydrocarbons, being formed, whilst the residue becomes still poorer in hydrogen. Several instances of this decomposition have been studied.
[With L. JEZIORANSKI.]—Two portions of the residue from Galician petroleum, remaining after the removal of all hydrocarbons boiling below 200° , were fractionally distilled, one at atmospheric pressure, the other under a pressure of 24—30 mm. The fractions thus obtained were again submitted to rectification. The distillates obtained under diminished pressure were practically unaltered by this second rectification. Those obtained at the ordinary pressure, on the other hand, began to boil at a much lower temperature than during the first distillation, more than 50 per cent. of each fraction passing over before the temperature was attained at which the fraction originally began to boil; thus a fraction which originally was collected between 315° and 330° , began to boil in the second rectification at 80° , and 30 per cent. of it passed over below 200° . The fractions obtained originally at the highest temperatures appear to yield the hydrocarbons of lowest boiling point. In another experiment, a heavy petroleum residue from Java petroleum, beginning to boil at 400° , was heated for some days in a flask connected with a reflux condenser, and the products of low boiling point were examined; these only amounted to a small percentage of the oil, and consisted of 41 per cent. of unsaturated and 59 per cent. of saturated hydrocarbons. Similar results were obtained by heating the oil in sealed tubes at 400° ; the residue contained a carbonaceous deposit.

[With H. GRÜNING.]—The oils obtained by “cracking” petroleum, in order to obtain oils suitable for burning, have a sp. gr. = 0.8769 at 15° , and consist chiefly of olefines and paraffins, members of both series containing from 6 to 10 atoms of carbon having been isolated. In addition to these, benzene, toluene, xylene, mesitylene and ψ -cumene were isolated as nitro-compounds. It is also probable that naphthenes were present in small quantities.

[With C. SCHNEIDER.]—The oils obtained by distilling heavy petro-

leum under a pressure of about 6 atmospheres (Krey, German Patent 37728) have a sp. gr. = 0.8301, and closely resemble the foregoing in composition. A. H.

Decomposition of Chloroform, Bromoform and Chloral by Aqueous Solutions of Potassium Hydroxide. By ALEXANDRE DESGREZ (*Compt. rend.*, 1897, 125, 780—782).—Chloroform is decomposed at the ordinary temperature by an aqueous solution of potassium hydroxide (1 : 8), the products being carbonic oxide, potassium chloride and water; the decomposition is accelerated by the action of light and also by heating gently. Solid potassium hydroxide does not decompose dry chloroform in a similar manner. Methylchloroform, phenylchloroform, methylenic chloride and carbon tetrachloride give no similar reaction with aqueous potash.

Bromoform decomposes in the same way as chloroform, but more slowly, by reason of its smaller solubility, and iodoform, being insoluble, is not decomposed at all. Chloral, on the other hand, is decomposed more rapidly than chloroform, the first stage in the reaction (production of potassium formate and chloroform) developing sufficient heat to accelerate the completion of the change.

Alkali carbonates and alkali hydrogen carbonates produce no analogous decomposition.

The liberation of carbonic oxide under the conditions specified is a much more characteristic reaction for chloroform than those commonly employed. C. H. B.

Electrolytic Preparation of Iodoform. By FRITZ FOERSTER and W. MEVES (*J. pr. Chem.*, 1897, [ii], 56, 353—363. Compare Elles and Herz, *Zeit. elektrochem.*, 4, 113).—The cell used was a battery-jar of 500 c.c. capacity, closed with an indiarubber bung. The electrodes were three parallel sheets of platinum foil; the middle one was the anode and had an area of 85 sq. cm.; the cathodes were enclosed in a wrapping of parchment paper. Between the electrodes were two tubes for leading in gas, and there was also a tube for leading away the gases evolved. A copper and a gas voltameter were also inserted in the circuit; the former for measuring the total amount of electricity that had passed during the experiment, whilst the latter made it possible to ascertain at any moment how the cell was working, the volume of gas evolved in it being compared with that evolved in the cell. The charge consisted of 400 c.c. of a solution containing 60 grams of potassium iodide, 20 grams of sodium carbonate and 80 c.c. of alcohol, the whole being kept at 60—65° by immersing the cell in a water bath at that temperature. The current density was as a rule 2 ampères per sq. dm., and to obtain a current of 2 ampères a potential difference of 2 volts was necessary. Every 8 ampère-hours the iodoform was removed, and the amount of potassium iodide to which it corresponded was added, together with 20 c.c. of alcohol.

The formation of iodoform takes place according to the equation, $C_2H_5O + H_2O + 10I = CHI_3 + 7HI + CO_2$; no formic acid could be detected. It will be seen that for every $7HI + CO_2$ formed at the anode $10KOH$ are formed at the cathode; the excess of $1KOH$ must be converted into carbonate by passing a slow current of carbonic anhydride

into the cell, so as to keep the colour of the solution pale yellow. In the presence of potassium hydroxide, considerable quantities of iodate are formed, and some acetic acid. When the proper precautions are observed, the yield of iodoform is equivalent to 80—90 per cent. of the electricity that has passed through the cell; it diminishes, however, when the potassium carbonate has accumulated largely in the solution. After a time, then, it is better to continue the electrolysis without further addition of potassium iodide; in this way, some 80 per cent. of the total iodide used can be converted into iodoform.

C. F. B.

Silver Cyanamide. By PAUL LEMOULT (*Compt. rend.*, 1897, 125, 782—784).—Silver cyanamide is obtained by adding an aqueous solution of cyanamide to an ammoniacal solution of silver nitrate, treating the precipitate with nitric acid, reprecipitating with ammonia, and repeating this process until a pure product is obtained. It is insoluble in water even when heated, but is slightly soluble in hot dilute ammonia.

The action of ammoniacal silver nitrate on cyanamide solution develops +9.64 Cal. The decomposition of silver cyanamide by nitric acid, absorbs -11.2 Cal., and from these and other experiments in which silver cyanamide was decomposed by hydrochloric acid, it follows that $C + N_2 + Ag_2 = CN_2Ag_2$ solid, absorbs -52.0 Cal. This value agrees with the explosive properties of silver cyanamide when heated in air. It is noteworthy, however, that, in absence of oxygen, it can be heated to 300° without undergoing any change.

C. H. B.

Chlorocyanuramide. By PAUL LEMOULT (*Compt. rend.*, 1897, 125, 822—824).—Chlorocyanuramide, $C_3N_3(NH_2)_2Cl$, obtained by the action of ammonia on cyanuric chloride, crystallises in very slender needles, very slightly soluble in water. Its heat of combustion as determined in the calorimetric bomb is 2758.2 cal., and hence the molecular heat of combustion is +401.3 Cal. at constant volume and +400.3 Cal. at constant pressure. Its heat of formation at constant pressure is, therefore, +25.6 Cal. and it follows that $C_3N_3Cl_3$ sol. + $4NH_3$ diss. = $2NH_4Cl$ diss. + $C_3N_3H_4Cl$ sol. develops +81.7 Cal. The formation of the chlorocyanuramide, which is intermediate between cyanuric chloride and cyanuramide, is to be attributed to its insolubility. When cyanuric chloride and aqueous ammonia are heated in a sealed tube at 150°, the former is completely converted into cyanuramide. It is noteworthy that the difference between the heats of formation of cyanuric chloride and chlorocyanuramide, 107.9 Cal., representing the thermal effect of the substitution of $2NH_2$ for $2Cl$, is practically identical with the corresponding value in the case of acetic acid.

C. H. B.

Preparation of Acetals. By EMIL FISCHER and GEORG GIEBE (*Ber.*, 1897, 30, 3053—3059).—Both aliphatic and aromatic aldehydes can be converted into the corresponding acetals by the aid of dilute solutions of hydrogen chloride in the requisite alcohol. Diethylacetal, diethylpropionacetal, and dimethylmethylal are readily obtained by the aid of 1 per cent. solutions of hydrogen chloride in alcohol.

To prepare *glycoldimethylacetal*, $OH \cdot CH_2 \cdot CH(OMe)_2$, a larger quantity of alcohol must be taken, and the mixture heated for a longer time; it

boils at 158—159° (corr.) and resembles glycoldiethylacetal in all its properties. Glucoside-like products were not obtained.

Acraldehyde with a 0.5 per cent. solution of hydrogen chloride in ethylic alcohol yields triethoxypropane. Acraldehyde dibromide does not readily react at the ordinary temperature with a 1 per cent. solution of hydrogen chloride in ethylic alcohol, but on heating at 100° for 40 hours, the substance, $\text{OEt} \cdot \text{C}_2\text{H}_3\text{Br} \cdot \text{CH}(\text{OEt})_2$, is obtained; it boils at 103—104° (corr.) under a pressure of 14 mm. and has a sp. gr. = 1.185 at 15°. Benzodiethylacetal is obtained when benzaldehyde is heated with the 1 per cent. solution for 60 hours at 100°; the yield is about 50 per cent. Nitrobenzaldehydes react more readily than benzaldehyde itself.

Paranitrobenzodimethylacetal, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OMe})_2$, distils at 294—296° (corr.) under a pressure of 774 mm. On cooling, it solidifies and then melts at 23—25°. The corresponding *orthonitro*-compound boils at 274—276° at a pressure of 762 mm., but is partially decomposed at the same time. Anisaldehyde reacts in pretty much the same manner as benzaldehyde; the *acetal* boils at 253° (corr.) under a pressure of 764 mm. Its sp. gr. = 1.078 at 14°.

Piperonaldimethylacetal boils at 271—272° (corr.) under 757 mm. pressure; the yield is only 35 per cent. of the theoretical.

Salicylaldehyde, parahydroxybenzaldehyde, and vanillin give little or no acetal when heated for several days with alcoholic hydrogen chloride. J. J. S.

Decomposition of Galactose. By ALFRED WOHL and ERNST LIST (*Ber.*, 1897, 30, 3101—3108).—It has been shown previously (Abstr., 1893, i, 292) that, when the oxime of *d*-glucose is converted into a nitrile and hydrogen cyanide subsequently abstracted, *d*-arabinose is formed. Further researches have now shown that when the oxime of *d*-galactose (Abstr., 1888, 40) is treated in a similar manner, the product is Fischer and Bromberg's lyxose (Abstr., 1896, i, 348). Galactosoxime was obtained by a method similar to that adopted for the preparation of glucosoxime (*loc. cit.*); when boiled with anhydrous sodium acetate and acetic anhydride, it yields *pentacetylgalactonic nitrile*. The dark-coloured substance which is thrown down when the product of the above reaction is poured into the requisite amount of sodium carbonate solution is washed well with water, extracted several times with ether, and the residue from the ethereal extract crystallised repeatedly from dilute alcohol. It forms colourless crystals, melts at 135° (uncorr.), and is only sparingly soluble in water, moderately in cold alcohol, readily in hot alcohol, benzene, ether, or chloroform. When treated with silver oxide and excess of ammonia, it yields the acetamide derivative which melts and decomposes at 222—226° (uncorr.); in most of its properties this compound resembles the acetamide derivative of *d*-arabinose. The corresponding pentose could not be obtained by exactly the same method as was used for the preparation of *d*-arabinose. The method adopted was as follows: the acetamide derivative (10 grams) was heated with 200 grams of N sulphuric acid and 600 grams of water for 2 hours in a reflux apparatus, and then heated with an excess of barium carbonate; the clear filtrate was evaporated

under reduced pressure to 20 c.c., diluted with 30 c.c. of 6 N sulphuric acid, extracted 15—20 times with ether in order to remove acetic acid, and the sulphuric acid precipitated with barium hydroxide, any excess of which was removed by the aid of carbonic anhydride. After filtration, the solution was evaporated under reduced pressure, when the sugar was obtained in the form of an uncrystallisable syrup. It gave the usual coloration with alkalis, reduced Fehling's solution, was lævoptatory, yielded fufuraldehyde on boiling with hydrochloric acid, and with phenylhydrazine gave xylosazone. Its identity with Fischer and Bromberg's lyxose was established by oxidising it to the lactone of lyxonic acid by Allen and Tollens' method (*Annalen*, 1891, 260, 306).
J. J. S.

Action of the Halogens on Aliphatic Amines and Preparation of their Perhaloids. By JAMES F. NORRIS (*Amer. Chem. J.*, 1898, 20, 51—64. Compare Abstr., 1896, i, 336).—The action of bromine and iodine on a number of aliphatic amines has been studied in order to determine whether the formation of iodine additive products and perbromides, such as those already described, is general. The action of iodine is being further investigated; so far, trimethylamine is the only amine which gives a di-iodo-additive product. Dimethylamine gives a compound containing two iodine atoms, but it has a constitution analogous to the bromides given below. Diamylamine gives the per-iodide $\text{NH}(\text{C}_5\text{H}_{11})_2\text{HI}_2$.

A number of perbromides have been obtained, all having the general structure $\text{NR}_3\cdot\text{HBr}\cdot\text{Br}$, where one R may be hydrogen, and all give off 1 atom of bromine when dissolved in water. Primary amines apparently do not form perbromides.

By the action of chlorine on trimethylamine, a very unstable compound, having the appearance and odour of camphor, was obtained, but it could not be purified or analysed.

Attempts to prepare the compound $\text{NMe}_3\cdot\text{ICl}$, described by Pictet and Kraft (Abstr., 1892, 1356), proved unsuccessful, as in all cases the product had the composition NMe_3I_2 .

[With E. H. LAWS.]—*Dimethylammonium dibromide*, prepared by the action of bromine on dimethylamine hydrobromide, separates from alcoholic solution in yellow needles which melt at 93° , and do not decompose when heated to 200° . Bromine is without further action; chlorine, however, displaces one bromine atom, forming a *chlorobromide*, $\text{NHMe}_2\cdot\text{HCl}\cdot\text{Br}$, which can also be prepared by the action of bromine on dimethylamine hydrochloride.

Dimethylammonium tri-iodide, obtained by the action of iodine on dimethylamine hydriodide, crystallises from ethylic acetate in long needles, with a dark blue, steely lustre, melts at 97° , is decomposed by water into the hydriodide and free iodine, whilst treatment with potassium hydroxide yields iododimethylamine $(\text{CH}_3)_2\text{NI}$. The *di-iodide* was obtained as a dark-coloured oil.

Dimethylammonium chloriodide, $\text{NHMe}_2\cdot\text{HCl}\cdot\text{I}$, prepared by the action of iodine on methylamine hydrochloride dissolved in alcohol and chloroform, crystallises in dark red needles melting at 100° . Water liberates all the iodine, and potassium hydroxide forms iododimethyl-

amine. When treated with chlorine, a substance, $\text{NHMe}_3, \text{HCl}, \text{I}, \text{Cl}_2$, is obtained crystallising from alcohol in yellow needles. The *bromiodide* is a dark red, crystalline salt melting at $98-99^\circ$.

[With F. M. SMALLEY.]—*Trimethylammonium chloriodides*. The salt containing two halogen atoms is obtained when iodine monochloride acts on trimethylamine, as dark, reddish-brown needles melting at 84° . Water liberates iodine. A second salt, of the composition $\text{NMe}_3, \text{HCl}, \text{ICl}_2$, is produced when iodine trichloride is used instead of the monochloride; this melts at 168° , and is decomposed by water, with liberation of chlorine and iodine. The *chlorobromide* crystallises in yellow needles, and dissolves in water with liberation of bromine; the *bromiodide*, which crystallises in maroon needles, melts at 89° , and gives up iodine when acted on by water.

[With A. E. KIMBERLY.]—*Diethylammonium dibromide* crystallises in reddish-yellow needles, and when treated with potassium hydroxide yields a heavy, yellow, insoluble oil, which is still under investigation. The corresponding *dipropyl* and *tripropyl* compounds are crystalline substances, and the *diamyl* compound is a red oil.

When bromine acts on trimethylamine or its hydrobromide, a red oil is obtained which cannot be purified without decomposition. Triethylamine is not acted on by bromine. A. W. C.

Crystalline Forms of the Platinochlorides of Diamines. By JOSEPH A. LE BEL (*Compt. rend.*, 1896, 125, 351—354).—The author has examined salts of the type $(\text{NH}_2\text{RR}')_2\text{PtCl}_6$, and also double salts such as $(\text{NH}_2\text{Me}_2, \text{NH}_2\text{Pr}_2)\text{PtCl}_6$. The following method was adopted in order to determine whether any two given diamines formed such a double salt. 0.1 gram of one platinochloride was mixed with an equivalent quantity of the platinochloride of the second, about three-fourths was allowed to crystallise, and the sp. gr. of the crystals determined by the aid of ethylenic dibromide which was diluted with light petroleum until the crystals floated in equilibrium. If no double salt was formed, the original compounds were present, and the densities were little altered. If the substance was a double salt, its sp. gr. lay between those of the two original salts. The densities, axial relations, $a:b:c$, and inclination β of a large number of the platinochlorides of diamines are given. J. J. S.

Constitution of Hexamethylenetetramine. By GEORG COHN (*J. pr. Chem.*, 1897, [ii], 56, 345—352).—The author proposes the formula $\text{CH}_2:\overset{\text{NH}}{\underset{\text{C}}{\text{C}}}>\text{CH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}\cdot\text{NH}$ as affording the best expression of the reactions of hexamethylenetetramine (which is obtained by the action of ammonia on formaldehyde), and shows how these reactions can be explained by its means. Incidentally, the formula $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}\cdot\text{NH}$ is assumed for trimethylenetriamine. The points of which a formula for hexamethylenetetramine must afford an explanation are (1), the relation of the substance to the sugar group; (2), the different function of the nitrogen atoms; (3), the numerous additive products and their different stability; (4), the formation of tri- and pent-amine derivatives. C. F. B.

Isonitramines, and their Resolution into Hyponitrous Acid.
By ARTHUR R. HANTZSCH and A. SAUER (*Annalen*, 1897, 299, 67—99. Compare Abstr., 1897, ii, 25).—Hydroxyurethane *benzyl ether*, $\text{COOEt}\cdot\text{NH}\cdot\text{OCH}_2\text{Ph}$, obtained by agitating ethylic chlorocarbonate with α -benzylhydroxylamine, crystallises from alcohol in white plates, and melts at 31° . The substance dissolves readily in ether, more sparingly, however, in alcohol, and with still greater difficulty in water. The *nitroso*-derivative boils at 106° under a pressure of 35 mm., and resists the action of cold acids; it decomposes when distilled in an atmosphere of steam. Aqueous and alcoholic alkalis resolve the *nitroso*-derivative into benzaldehyde and ethylic alcohol, nitrogen and carbonic anhydride being eliminated.

Benzenesulphonhydroxamic acid *benzyl ether*, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{OCH}_2\text{Ph}$, is prepared from benzenesulphonhydroxamic acid (Piloty, Abstr., 1896, i, 555) and α -benzylhydroxylamine; it crystallises from alcohol in white needles, and melts at 107° . The impure *nitroso*-derivative, which could not be isolated, yields benzaldehyde and nitrogen when treated with sodium carbonate.

Attempts to prepare the *nitroso*-derivative of hydroxyurethane (Hantzsch, Abstr., 1894, i, 364) were also unsuccessful, treatment of hydroxyurethane with nitrous acid giving rise to a yellow oil which decomposes in the desiccator; aqueous ammonia dissolves the oil, with liberation of nitrogen, acetaldehyde being produced. Benzhydroxamic acid and acethydroxamic acids, however, yield no isonitramine, nitrous acid converting them into hydroxylamine and benzoic and acetic acids respectively; hyponitrous acid was not recognised among the products, nor was this substance produced by the action of nitrous acid on benzenesulphonhydroxamic acid.

Dimethylamidocarboxylic chloride, $\text{NMe}_2\cdot\text{COCl}$, is prepared by passing dry carbonyl chloride over dry dimethylamine hydrochloride, which is carefully heated in a small distilling flask, the receiver being cooled with ice; it is a colourless liquid which boils at 165° , and is indifferent towards alkalis at 0° , being resolved into carbonic anhydride and dimethylamine hydrochloride when heated. On agitating the substance with free, aqueous hydroxylamine, the liquid acquires the properties of a hydroxamic acid. It develops an intense violet coloration with ferric chloride, reduces silver nitrate, and yields a slimy, green copper salt; the dimethylhydroxycarbamide has not been isolated. The *benzyl ether*, $\text{NMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OCH}_2\text{Ph}$, is an oil which does not solidify at -15° ; the *hydrochloride* is precipitated on passing hydrogen chloride into its ethereal solution.

Dimethylnitrosohydroxycarbamide (*dimethylcarbonylisonitramine*), $\text{NMe}_2\cdot\text{CO}\cdot\text{N}\cdot\text{N}_2\text{O}_2\text{H}$, is prepared by passing nitrous anhydride into the liquid obtained by agitating dimethylamidocarboxylic chloride with hydroxylamine until it no longer develops colour with ferric chloride; it is a yellow oil, which mixes in every proportion with water, being extracted from the solution by ether. It decomposes when gently heated. Although indifferent towards acids, the substance is very sensitive towards alkalis, caustic potash converting it into potassium hyponitrite and dimethylamine, with elimination of carbonic anhydride, and it is decomposed also by ammonia.

Diethylamidocarboxylic chloride, $\text{NEt}_2\cdot\text{COCl}$, boils at 186° , and in behaviour resembles the methyl-derivative.

When carbonyl chloride is passed into an ice cold solution of hydroxylamine, the liquid acquires the properties of a hydroxamic acid, but the product is very unstable. It is immaterial whether one molecular proportion of hydroxylamine is employed, or twice this amount, the liquid in each case developing an intense violet coloration with ferric chloride, and yielding with copper acetate a highly unstable copper salt which liberates gas, and passes into cuprous oxide. These facts point to the formation of *hydroxycarbaminic*, $\text{OH}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, or *carbohydroxamic acid*, $(\text{OH})_2\cdot\text{C}\cdot\text{NOH}$, instead of dihydroxycarbamide, $\text{CO}(\text{NH}\cdot\text{OH})_2$.

On treating with nitrous acid the liquid obtained by the action of carbonyl chloride on aqueous hydroxylamine, carbonic anhydride, nitrous oxide, and water are produced. If, however, the operation is carried out in methylic alcohol, evidence of the production of hyponitrous acid is forthcoming.

The authors have estimated the amount of ammonia arising from the decomposition of hyponitrous acid, and find that the quantity is variable and very small; it probably arises from ammonium salts contaminating the silver hyponitrite from which the free acid is prepared. Contrary to the statement of Thum (Abstr., 1894, ii, 13), it is not possible to estimate hyponitrous acid by titration with potassium permanganate.

Hyponitrous acid is obtained by the action of nitrous acid on hydroxylamine or hydroxycarbamide dissolved in methylic alcohol.

M. O. F.

Salts of Nitroparaffins, and Acylated Derivatives of Hydroxylamine. By LAUDER W. JONES (*Amer. Chem. J.*, 1898, 20, 1—51. Compare Abstr., 1896, i, 460).—When sodium isonitroethane, prepared by the action of sodium ethoxide on an alcoholic solution of nitroethane, is acted on by benzoic chloride in aqueous or ethereal solution, a very complicated mixture of substances is produced. In the first place, a derivative, $\text{CHMe}\cdot\text{NO}\cdot\text{OBz}$, of isonitroethane is formed by replacement of sodium by the benzoyl group; this cannot be isolated, but is immediately converted by intramolecular oxidation into the *benzoate of acethydroxamic acid*, $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{OBz}$, existing in two forms, which can be separated by the difference in their solubility in ether; the one forms well developed crystals melting at 98 — 99° , the other flat, transparent crystals melting at 69 — 70° . After a time, the form of lower melting point, which is possibly a hydroximic acid, becomes opaque, and passes completely into the form of high melting point. It is decomposed by boiling water or dilute alkalis into benzoic acid and acethydroxamic acid, and on heating yields benzoic acid, methylcarbimide, and a brown residue. A specimen of the benzoate prepared by the action of benzoic chloride on pure acethydroxamic acid was also found to exist in two modifications corresponding exactly in melting points and crystalline forms with the above.

In the original reaction, this benzoate immediately acts on the isonitroparaffin salt, regenerating nitroethane and forming the sodium

salt of the benzoate of acethydroxamic acid, and the latter, in presence of benzoic chloride, reacts in two ways, giving rise:—(1) to the *benzoate of benzoylacethydroxamic acid*, $\text{OBz}\cdot\text{CMe}\cdot\text{N}\cdot\text{OBz}$, a thick oil that could not be made to crystallise; this is decomposed by alcoholic potash into benzoic acid and the benzoate of acethydroxamic acid, thus proving its constitution, and:—(2) to *α -benzoyl- β -acetylbenzoylhydroxylamine*, $\text{NAcBz}\cdot\text{OBz}$, a neutral substance occurring in transparent, monoclinic crystals melting at $68\text{--}69^\circ$; this is insoluble in alkalis and water, but soluble in alcohol, ether, and light petroleum. On treatment with alcoholic potash, it is converted into the benzoate of benzhydroxamic acid and acetic acid, which fact, in conjunction with the synthesis of this hydroxylamine derivative from the benzoate of benzhydroxamic acid and acetic chloride, conclusively proves its constitution. *Acetobenzhydroxamic benzoate*, $\text{OBz}\cdot\text{N}\cdot\text{CPh}\cdot\text{OAc}$, forms needle-shaped crystals melting at $84\text{--}85^\circ$, soluble in alcohol and ether, but insoluble in water.

It was expected that the results obtained by the action of ethylic chlorocarbonate on isonitroethane would be similar to those of the action of benzoic chloride; but although derivatives of acethydroxamic acid are produced, the reaction is complicated by the evolution of carbonic anhydride, and has not been thoroughly investigated. In order, however, to become acquainted with the possible derivatives, the following compounds were prepared synthetically.

Ethylic acethydroxamic carbonate, $\text{CMe}\cdot\text{NH}\cdot\text{O}\cdot\text{COOEt}$, prepared by the action of ethylic chlorocarbonate on acethydroxamic acid, crystallises from ether in long, flat needles melting at $71\text{--}72^\circ$. When left in contact with ferric chloride, it shows an intense colour reaction, is decomposed by alkalis and alkali carbonates, and on distillation gives carbonic anhydride, an intense odour of a carbimide, and a pale yellow oil boiling between 180 and 220° .

Ethylic ethylnitrolic carbonate, $\text{NO}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{O}\cdot\text{COOEt}$, is a yellow oil boiling at $143\text{--}144^\circ$ (17 mm.), or with considerable decomposition at $210\text{--}215^\circ$ under the ordinary pressure. Boiling water decomposes it, liberating carbonic anhydride and forming ethylnitrolic acid and its decomposition products.

The action of benzoic chloride on sodium isonitromethane presents difficulties which have not yet been overcome, but there is no doubt that the benzoate of benzoylformhydroxamic acid is produced with formation of a similar salt of formhydroxamic acid as intermediate product.

Formhydroxamic acid, $\text{COH}\cdot\text{NH}\cdot\text{OH}$, prepared by the action of ethylic formate on a mixture of hydroxylamine hydrochloride and sodium methoxide, crystallises in large, thin, transparent plates with a brilliant pearly lustre and striated surfaces, and melts at $81\text{--}82^\circ$. It is soluble in warm acetone, from which it can be obtained in groups of thick crystals, but on standing these redissolve, undergoing decomposition, the exact nature of which has not been fully determined. The pure acid is not hygroscopic, and is stable, but when heated slightly above its melting point it explodes, giving off a vapour smelling strongly of hydroxylamine; this fact, taken in conjunction with its stability, supports the above oxam-formula rather than the oxime form, $\text{OH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$. The *sodium* salt prepared by the action of sodium ethoxide on an alco-

holic solution of the acid, separates as a fine, white, very hygroscopic powder, which explodes on heating; the *copper*, *lead*, and *mercury* salts are also explosive. The *benzoate*, prepared by the action of benzoic chloride on the acid, crystallises from ether in well developed prismatic needles melting at $76.5-77.5^{\circ}$; it is decomposed by caustic soda into benzoic and formhydroxamic acids, and by heat into benzoic acid and carbimide. During the preparation of this benzoate, *benzoylformhydroxamic benzoate*, $\text{OBz}\cdot\text{CH}\cdot\text{N}\cdot\text{OBz}$, is also obtained; this crystallises from a mixture of ether and light petroleum in delicate, colourless needles melting at $109-111^{\circ}$. It is insoluble in alkalis, but is decomposed by them, more especially on heating.

Experiments on the action of mercuric chloride on sodium isonitromethane, and of the action of alkylic iodides on the mercury salts thus formed, are described; it is shown that these salts cannot be derivatives of carbonic anhydride oxime of the formula $\text{CO}\cdot\text{N}\cdot\text{OH}$, as was considered probable by Nef.

In discussing the formulæ of the salts of the nitroparaffins, the author points out that it is impossible to explain their reactions and properties, more especially the intramolecular oxidation which they undergo, if the ring grouping proposed by Hantzsch (Abstr., 1896, i, 353, 672) is adhered to. He therefore assigns to them Nef's open formulæ (*ibid.*, 461).

Hydroxyurethane (carbethoxyhydroxamic) methylic ether,
 $\text{EtO}\cdot\text{CO}\cdot\text{NH}\cdot\text{OMe}$,

is formed when methylic iodide acts on the potassium derivative of hydroxyurethane prepared by a slight modification of the method employed by Hantzsch (Abstr., 1894, i, 364); it is a colourless liquid boiling at $186-188^{\circ}$, and gives no reaction with ferric chloride. When treated with concentrated hydrochloric acid, it is decomposed into carbonic anhydride, ethylic chloride, and α -methylhydroxylamine hydrochloride. The corresponding *ethylic* ether boils at $195-196^{\circ}$ ($95-97^{\circ}$ at 17 mm.); hydrochloric acid decomposes it into carbonic anhydride, ethylic chloride, and α -ethylhydroxylamine hydrochloride. It was hoped that ethers of the oxime of carbonic anhydride would be obtained by the action of phosphorus pentachloride on this substance, but owing to the instability of the product, it has been impossible to decide this point. The *benzyllic* ether, a thick, colourless oil boiling at $171-172^{\circ}$ (11 mm.), is soluble in alkalis, and is reprecipitated undecomposed by acids; concentrated hydrochloric acid decomposes it with production of α -benzylhydroxylamine hydrochloride. The *benzoate* forms soft, fibrous crystals melting at $38-39^{\circ}$ and boiling at $180-190^{\circ}$ (20 mm.); when treated with benzoic chloride, it is converted into the dibenzoyl derivative of hydroxyurethane, which separates from a mixture of ether and light petroleum in transparent, prismatic crystals melting at $72-73^{\circ}$.

$\alpha\beta$ -*Dimethylcarbethoxyhydroxylamine* [*hydroxymethylurethane methylic ether*], $\text{COOEt}\cdot\text{NMe}\cdot\text{OMe}$, is also produced by the action of methylic iodide on carbethoxyhydroxamic acid as a colourless oil boiling at $150-155^{\circ}$; when treated with concentrated hydrochloric acid, carbonic anhydride, ethylic chloride, and α -dimethylhydroxylamine hydrochloride, $\text{NHMe}\cdot\text{OMe}$, HCl , are produced. The latter crystallises from

chloroform in long, coarse, prismatic needles melting at $115-116^{\circ}$; it is not hygroscopic, is volatile at 100° , and does not reduce ammoniacal silver nitrate or Fehling's solution. The *platinochloride* separates from alcohol in red, prismatic crystals melting and decomposing at 180° . The *free base* is a colourless, very volatile liquid, boiling at $42.2-42.6^{\circ}$, of a sweet, rather unpleasant odour, and does not reduce silver nitrate or Fehling's solution.

$\alpha\beta$ -Diethylcarboxyhydroxylamine [*hydroxyethylurethane ethylic ether*] *hydrochloride* is with difficulty obtained in long, fibrous needles melting at $123-124^{\circ}$. The *free base* is an oil boiling between 160° and 180° .
A. W. C.

The Direct Elimination of Carbonic Oxide, and the Reaction of this with Water. By CARL ENGLER and J. GRIMM (*Ber.*, 1897, 30, 2921—2926. Compare Abstr., 1893, i, 512).—Many organic compounds decompose when heated, carbonic oxide being formed directly, without any reduction of carbonic anhydride (compare Phillips, *Trans. Amer. Phil. Soc.*, 17, 1). Formic acid, for instance, at $150-160^{\circ}$ yields a gas which consists of 98.8 of carbonic oxide and 1.2 per cent. of carbonic anhydride. Ethylic formate decomposes at 300° , yielding a mixture of carbonic oxide, 18.2; carbonic anhydride, 29.5; ethylene, 7.2, and hydrogen, 45.1 per cent.: amyl formate decomposes in a similar manner at 300° , but yields amylene instead of ethylene, whilst ethylic oxalate at 200° yields carbonic oxide, 48.4; carbonic anhydride, 43.8, and olefines, 7.8 per cent.

Benzoin at 280° yields a gas containing 92 per cent. of carbonic anhydride and 8 of carbonic oxide; the oily residue produced in this case contains diphenylmethane, deoxybenzoin, benzil, and a trace of benzaldehyde. Benzoylacetone does not yield any gas at 300° .

Pure carbonic oxide, carefully freed from oxygen, does not react with water vapour at 250° , but does react at 300° , producing carbonic anhydride. It is probable that the formation of carbonic anhydride in the foregoing decompositions of various substances is due to this secondary reaction between the carbonic oxide, which is first produced, and water vapour.
A. H.

Volatile Acids of the Acetic Series from the Suint of Wool. By A. BUISINE and P. BUISINE (*Compt. rend.*, 1897, 125, 777—780).—When the water used for the desuintage of wools is allowed to remain exposed to the air for a few days, it undergoes, as the authors have previously shown, a special fermentation which results in the formation of volatile acids of the acetic series. After fermentation, one sample of sp. gr. = 1.079 was found to have the following composition per litre: total residue, 153.4; ammonia (as carbonate), 1.5; total nitrogen, 4.5; potassium carbonate (as such), 7.6; volatile acids (calculated as H_2SO_4), 16.0; fatty matter, 15.5; inorganic matter, 77.4; total potassium carbonate obtainable, 65.5 grams.

In order to extract the fatty acids, the liquid is boiled to expel ammonia, which is collected, and is then acidified with sulphuric acid, and treated with a current of steam, the acids of higher molecular weight distilling first. The percentage composition of the acid mixture obtained from the suint referred to above was acetic acid, 60; pro-

pionic acid, 25 ; butyric acid, 5 ; valeric acid, 4 ; caproic [hexoic] acid, 3 ; benzoic acid, 3, and traces of formic and caprylic [octoic] acids and phenol, the total yield per litre being 20.6 grams. The crude mixture of acids is very suitable for the production of "acetone oil."

The acetic acid can be separated by adding to an aqueous solution of the mixed acids a limited quantity of calcium carbonate, which combines exclusively with the acetic acid, and the other acids can be distilled off in a current of steam.

The sulphuric acid is removed as potassium sulphate by concentrating the liquid from which the acids have been removed, or the residue from this liquid may be mixed with calcium carbonate before being heated. In the latter case, on treatment with water, all the potassium dissolves as carbonate and the sulphuric acid remains undissolved as calcium sulphate.

C. H. B.

Conversion of Butyric into Isobutyric Acid. By EMIL ERLÉNMEYER, sen. (*Ber.*, 1897, 30, 2956—2962. Compare Hutzler and V. Meyer, this vol., i, 62).—The author admits that he is not certain that the calcium butyrate used by him was free from isobutyrate; he thinks it probable, however, that the calcium salt obtained by Hutzler and V. Meyer, which in appearance and properties resembled calcium butyrate, was a double isobutyrate and butyrate. To show that the conversion of butyrate into isobutyrate may take place, the author refers to the conversion of benzil into benzilic acid. of pinacone into pinacoline, reactions in which OH changes place with H. It is considered that a similar interchange between CH_3 and H may also be possible, for example, the formation of isopropyl alcohol from normal propylamine (*Annalen*, 1876, 181, 128, and this Journal, 1876, ii, 182), and the conversion of normal propyl bromide into isopropyl bromide by the aid of aluminium bromide (*Ber.*, 1879, 12, 2279) are cited as cases.

J. J. S.

A seemingly General Reaction of α -Amido-acids of the Formula $\text{NH}_2\cdot\text{CHR}\cdot\text{COOH}$. By EMIL ERLÉNMEYER, jun. (*Ber.*, 1897, 30, 2896—2899. Compare Abstr., 1896, i, 305; 1897, i, 480).—The behaviour of glycocine towards benzaldehyde (*loc. cit.*) is exhibited also by other α -amido acids, such as aspartic acid, leucine, and tyrosine.

M. O. F.

Stereoisomeric Chlorobromosuccinic Acids. By PAUL WALDEN (*Ber.*, 1897, 30, 2883—2888).—*Fumaroid chlorobromosuccinic acid*, $\text{COOH}\cdot\text{CHCl}\cdot\text{CHBr}\cdot\text{COOH}$, is prepared by heating chlorofumaric acid with a solution of hydrogen bromide in glacial acetic acid at 125° until completely dissolved, and subsequently at 135 — 140° during 2 hours; it melts and decomposes at 235 — 237° in a sealed capillary tube. When mixed with phosphoric anhydride and distilled, the acid yields chloromaleic acid, which is also produced, along with chlorofumaric acid, when chlorobromosuccinic acid is boiled with water (5 parts); methylic alcoholic potash converts it into mesotartaric acid. The *ethylic* salt is prepared by warming the acid with ethylic alcohol and a small quantity of concentrated sulphuric acid, and it is also produced when ethylic chlorofumarate is heated on the water bath with a fuming solution of

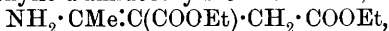
hydrogen bromide in glacial acetic acid; it crystallises from petroleum in feathery aggregates of small needles, and melts at 59—60°.

Maleinoid chlorobromosuccinic acid is prepared by saturating with chlorine a solution of bromine in chloroform, adding maleic anhydride, again passing chlorine into the liquid, which is then exposed to bright sunlight; the anhydride which is obtained on evaporating the chloroform yields the acid when dissolved in cold water. The acid crystallises from water or ethylic acetate in plates, and dissolves readily in common solvents; it melts and decomposes at 165° when heated in a sealed capillary tube. Distillation with phosphoric anhydride converts it into chloromaleic acid, and protracted treatment with boiling water gives rise to chlorofumaric acid; when gently heated with fuming hydrochloric acid, it is converted into fumaroid chlorobromosuccinic acid. The *anhydride* crystallises from chloroform, and melts at 78°; the *ethylic* salt is an oily liquid.

Directions for the preparation of chloromaleic and bromomaleic acids are given in the paper, which concludes with a synopsis of the behaviour of dibromosuccinic, dichlorosuccinic, chlorobromosuccinic (fumaroid and maleinoid), isodibromosuccinic, and isodichlorosuccinic acids and their derivatives.

M. O. F.

***α*-Amidoethylidenesuccinimide and Acetylsuccinimide.** By ICILIO GUARESCHI (*Chem. Centr.*, 1897, i, 283; from *Atti Real. Accad. Torino*, 31).—Ethylic *α*-amidoethylidenesuccinate,



was obtained by Conrad and Epstein (*Abstr.*, 1888, 253) from ethylic acetylsuccinate by the action of gaseous ammonia, and by Emery (*Abstr.*, 1891, 544) from the same substance by saturated alcoholic ammonia at 0°. The author finds, however, that when aqueous ammonia (sp. gr. = 0.914) is used, *α*-amidoethylidenesuccinimide,

$\text{NH}_2 \cdot \text{CMe} : \text{C} \begin{array}{l} \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{array} > \text{NH}$, is formed; this crystallises from water in prisms, and when heated darkens at 235—240° and melts at 274—275°. It is readily soluble in boiling water, sparingly in cold water and in alcohol, and nearly insoluble in ether. The *silver* derivative of the imide was analysed. On treating this with hydrochloric acid, am-

monium chloride and *acetylsuccinimide*, $\text{CHAc} \cdot \text{CO} \begin{array}{l} \text{CH}_2 - \text{CO} \end{array} > \text{NH}$, were obtained; the latter melts at 84—87°, and yields a *silver* derivative. No well-characterised ethyl derivative of *α*-amidoethylidenesuccinimide could be obtained, but an *acetyl* derivative was prepared; this crystallises from hot water in long needles, melts at 233—234°, and gives rise to a *silver* derivative, which, however, was not obtained pure.

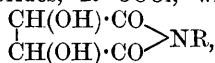
W. A. D.

Some Pyrotartaric Alkylimides. Condensation of Tartaric Alkylimides with Acid Chlorides. By M. KLING (*Ber.*, 1897, 30,

3039—3043).—The pyrotartaric alkylimides, $\text{CHMe} \cdot \text{CO} \begin{array}{l} \text{CH}_2 - \text{CO} \end{array} > \text{NR}$, are made by distilling the amine hydrogen salt with a certain excess of the amine. *Pyrotartarmethylimide* comes over at 223°; pyrotartar-

ethylimide boils at 222—223°, the yellowish *pyrotartarbenzylimide* at 315°, and *pyrotartarphenylimide* melts at 107°.

By heating acid chlorides, $R' \cdot \text{COCl}$, with tartarimides,



at 100°, derivatives of the type $\begin{array}{c} R' \cdot \text{COO} \cdot \text{CH} \cdot \text{CO} \\ | \\ R' \cdot \text{COO} \cdot \text{CH} \cdot \text{CO} \end{array} \text{>NR}$ are obtained.

Dibenzoyltartarethylimide melts at 159—160°; *phthalyltartarmethylimide* begins to melt and decompose at 180°. *Dicinnamoyltartarmethylimide* crystallises with benzene (1 mol.), and then melts at 80—81°; after the benzene has been driven off, it forms a vitreous mass which melts at 70—72°. This is named the α -variety; when crystallised from alcohol, or after prolonged lying in the air, it is obtained in crystals which melt at 95°, and are termed the β -variety; this is reconverted into the α -form by simple heating above its melting point. In 10 per cent. ethylic acetate solution, the α - and β -forms have the rotatory power 307.8° and 311.6° respectively. Two similarly isomeric dibenzoyltartarmethylimides have been described by Ladenburg (Abstr., 1897, i, 139).
C. F. B.

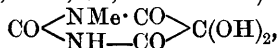
Interconversion of Optical Antipodes. By PAUL WALDEN (*Ber.*, 1897, 30, 3146—3151. Compare this vol., i, 176).—The action of silver carbonate on optically active halogen derivatives of succinic acid in aqueous solution converts them into malic acids which rotate the plane of polarisation in the same directions as the respective halogen derivatives. Alcoholic potash of certain concentration (1 : 4) eliminates halogen hydride, giving rise to inactive products, and reduction with sodium amalgam, in alcoholic solution, likewise yields an inactive solution. If, however, halogen is replaced by hydroxyl through the agency of less concentrated alcoholic potash (1 : 9), the optical antipodes of the malic acids obtained by the action of silver salts are produced. Aqueous potash and baryta have the same effect as alcoholic potash.

M. O. F.

Action of Formaldehyde on Carbamide. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, 21, 460. Compare Abstr., 1897, i, 22).—Carbamide, when allowed to remain with an excess of formaldehyde (40 per cent. solution) in alkaline solution, yields a white precipitate, $\text{C}_3\text{N}_2\text{O}_3\text{H}_8 = \text{CO}(\text{NH} \cdot \text{CH}_2 \cdot \text{OH})_2$, which is soluble in hot water, and is precipitated by alcohol as a gelatinous mass. After two recrystallisations from water, it appears to be transformed into the compound $\text{C}_6\text{N}_4\text{O}_5\text{H}_{14}$.

In a neutral solution, the chief products are the above-mentioned soluble compound, $\text{C}_3\text{N}_2\text{O}_3\text{H}_8$, and a substance, $\text{C}_5\text{N}_4\text{H}_{12}\text{O}_4$, which is insoluble in water.
J. J. S.

1-Methyl- and 1:7-Dimethyl-uric Acids. By EMIL FISCHER and HANS CLEMM (*Ber.*, 1897, 30, 3089—3097).—Methylalloxan,



(compare Hill, this Journal, 1876, ii, 509; and Fischer, Abstr., 1883, 356), which is best obtained by the oxidation of theobromine with hydrochloric

acid and potassium chlorate, may be isolated, by the aid of hydrogen sulphide, as dimethylalloxantin, which, after recrystallisation from water, is carefully oxidised by nitric acid back to methylalloxan. When its solution is evaporated under diminished pressure, methylalloxan crystallises in large, colourless, compact crystals; it turns red at about 100° and melts and decomposes at 156°.

1-Methyluramil, $\text{CO} \begin{array}{c} \text{NMe} \cdot \text{CO} \\ \text{NH} - \text{CO} \end{array} \text{CH} \cdot \text{NH}_2$, is obtained when methylalloxan (4 parts) is treated with a concentrated solution of ammonium sulphite (12 parts) for 6 hours at 80°. If rapidly recrystallised from hot water, it forms colourless plates, which, when moist, readily turn red. In its properties it resembles dimethyluramil (Techow, Abstr., 1895, i, 83).

When 1-methyluramil (1 part) is heated with pure potassium cyanate (1 part) and water (3 parts) on the water bath for some 5—10 minutes, until the deep red colour first produced disappears, and the mixture is then allowed to cool, *potassium methyl-ψ-urate* separates. The free acid crystallises from hot water in small, colourless needles, turns red at 200°, and melts and decomposes at about 220°. The yield is almost quantitative.

1-Methyluric acid is obtained when the pseudo-acid is boiled for a few minutes with 9 times its weight of 20 per cent. hydrochloric acid, and then heated on the water bath for an hour. The precipitated acid is best purified by conversion into its *magnesium* salt, $\text{C}_{12}\text{H}_{10}\text{N}_8\text{O}_6\text{Mg} + 7\text{H}_2\text{O}$, which can be readily recrystallised from boiling water. The acid crystallises in minute needles, turns brown at about 400°, and is carbonised at higher temperatures without melting; its extremely slight solubility in hot water (1 in 2050) differentiates it from 3-methyluric acid. The acid dissolves in an excess of caustic alkali, in warm ammonia, and in hot dilute barium hydroxide solutions. It is readily oxidised by nitric acid or chlorine water, and gives the murexide reaction. The authors consider that von Loebe's acid (this vol., i, 128) is merely a mixture of their acid with 3-methyluric acid.

1:3-Dimethyluric acid is obtained when the 1-methyl acid (1 gram) is dissolved in 1 c.c. of N potassium hydroxide, and is shaken with 0.8 gram of methyl iodide at 50° for $\frac{3}{4}$ —1 hour; on adding hydrochloric acid, the dimethyl acid is precipitated together with a small quantity of the original monomethyl acid. The dimethyl acid is readily separated by solution in boiling water, and is identical with γ-dimethyluric acid prepared by Fischer and Ach (Abstr., 1896, i, 12). A mixture of 1:7-dimethyluramil and 1-methyluramil is obtained by the action of methylamine sulphite on methylalloxan; when the crude mixture is treated with potassium cyanate, a mixture of mono- and di-methyl-ψ-uric acids is obtained, and this, when warmed on the water bath for 2 hours with 20 per cent. hydrochloric acid, yields a mixture of 1-methyluric acid, and 1:7-dimethyluric acids. The dimethyl acid is much more readily soluble in boiling water (1 in 114) than the monomethyl acid; it crystallises in pointed prisms, often arranged in stars, and melts and decomposes at 390°. The *potassium*

salt, $C_7H_7N_4O_3K + H_2O$, is characteristic; the ammonium, barium, and silver salts are also described. J. J. S.

Tetramethyluric Acid. By EMIL FISCHER (*Ber.*, 1897, 30, 3009—3014. Compare Abstr., 1884, 1310).—This acid, $C_9H_{12}N_4O_3$, is now found to melt at 223° (corr. 228°). It is monoclinic; $a:b:c = 1.7686:1:2.0079$; $\beta = 61^\circ 20'$. When heated with 5 times its weight of phosphorus oxychloride for at least 10 hours at 160° in a sealed tube, it yields chlorocaffeine, $C_8H_9N_4O_2Cl$, melting at 186 — 188° ; this is best isolated by evaporating the product of the action, extracting the residue with water, heating this second residue with 5 times its weight of hydrochloric acid (sp. gr. = 1.19) for 3 hours at 130° , evaporating the whole to dryness, extracting the residue with dilute aqueous soda, and crystallising what is left from alcohol. By passing chlorine into a 1 per cent. aqueous solution of tetramethyluric acid at 25° , allocaffeine is obtained; this is now found to melt at 203° (corr. 206°). By passing dry chlorine into a 5 per cent. solution of the acid in dry chloroform free from alcohol, an *oxytetramethyluric acid*, $C_9H_{12}N_4O_4$, melting at 224° (corr. 229°), is obtained. When tetramethyluric acid (1 mol.) is shaken for 3 hours at 15° with normal potassium hydroxide solution (2 mols.), a basic substance is obtained which melts at 165 — 167° (corr. 166 — 168°); this has the composition $C_8H_{14}N_4O_2$, and hence stands to tetramethyluric acid in the same relation as caffeidine to caffeine; for this reason it is named *tetramethylureidine*. C. F. B.

Constitution of Hexahydrobenzene. By NIC. KIJNER (*J. pr. Chem.*, 1897, [ii], 56, 364—372).—The author adduces further arguments in support of the identity of hexahydrobenzene with methylpentamethylene, and complains that his early recognition of this identity has been ignored. Fresh samples of hexahydrobenzene have been prepared by heating benzene with hydriodic acid of sp. gr. = 1.96 for 24 hours at 280° , and purifying the product by treatment with nitric acid; one boiled at 72 — 73° under 752 mm. pressure, had a sp. gr. = 0.7489 at $20^\circ/0^\circ$ and index of refraction $n_D = 1.4101$ at 20° ; the other boiled at 71 — 73° , and had a sp. gr. = 0.7648 at $0^\circ/0^\circ$, 0.7486 at $20^\circ/0^\circ$. Prolonged action of fuming nitric acid at 0° appears to convert hexahydrobenzene partially into formic, acetic, and glutaric acids; the dilute acid at 100° converts it into the nitro-derivative, $\begin{matrix} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{matrix} > CMe \cdot NO_2$ of Markownikoff and Konow-aloff (Abstr., 1895, i, 454). When aniline is reduced with hydriodic acid at temperatures approaching 300° , the product distils between 65° and 81° , and probably contains some hexamethylene in addition to hexahydrobenzene (methylpentamethylene). C. F. B.

Migration of the Iodine Atom during the Nitration of Aromatic Iodo-Derivatives. By FRÉDÉRIC REVERDIN (*Ber.*, 1897, 30, 2999—3003. Compare Abstr., 1896, i, 475; 1897, i, 27).—The method of nitration adopted was to mix the derivative with nitric acid

of sp. gr. = 1.51 (usually with its own weight), and pour the mixture on to ice after a time. The iodonitrotoluene melting at 103° obtained by Beilstein and Kuhlberg (*Annalen*, 158, 347) by nitrating orthiodotoluene, is now shown to have the constitution $[\text{Me} : \text{I} : \text{NO}_2 = 1 : 2 : 5]$, for it is identical with the product obtained by the diazo-reaction from 1 : 2 : 5-nitrotoluidine. From 1 : 2 : 4-nitrotoluidine, 1 : 2 : 4-iodonitrotoluene was obtained; this is yellowish and melts at 51°. Pariodotoluene, when nitrated, yields iodonitrotoluene $[\text{Me} : \text{I} : \text{NO}_2 = 1 : 4 : 2]$ as the main product, together with paranitrotoluene, a lemon-yellow substance (? di-iodonitrotoluene) melting at 112°, and an oil; no migration of the iodine atom from the para- to the ortho-position takes place, such as is observed when pariodanisole and phenetole are nitrated.

The action of nitric acid on orth- and par-iodaniline and on pariodophenol results in the elimination of the iodine. From pariodacetanilide, the nitro-derivative of Michael and Norton (*Abstr.*, 1878, 406) could not be obtained.

Methylic orthiodobenzoate, when nitrated, yields pale yellow *methylic iodonitrobenzoate* melting at 123°. From methylic pariodobenzoate another methylic iodonitrobenzoate was obtained; this is yellow, but melts at 103.5°, and is therefore isomeric, and not identical, with the compound already described; no migration of the iodine atom to the ortho-position can have taken place.

C. F. B.

Double Salts of the Anilides with Cuprous Chloride and Cuprous Bromide. BY WILLIAM J. COMSTOCK (*Amer. Chem. J.*, 1898, 20, 77—79).—In studying the behaviour of certain of "Schiff's bases" towards cuprous chloride and bromide, the author wished to prepare derivatives of cuprous haloids which should be easily soluble in organic solvents and give up the haloids readily, and finds that the double salts with acetanilide fulfil these conditions.

The *double* salt of cuprous chloride and acetanilide has the composition $(\text{NHPh} \cdot \text{COMe})_2 \cdot \text{HCl} \cdot \text{CuCl}$, and is best prepared by adding its constituents to a hot mixture of glacial acetic and hydrochloric acids; it crystallises from alcohol in beautiful, long prisms. Protracted boiling of the solution, however, causes the acetyl group to separate. When heated, it darkens at 140° and melts near 170° with violent decomposition. Freshly prepared, it is colourless, but when dry, acquires a yellowish tint. It does not lose hydrogen chloride in a vacuum over caustic potash, and can be heated at 100° without loss in weight. The *double* salt with cuprous bromide crystallises from alcohol in long, colourless, doubly terminated prisms, darkening when heated to 170°, and melting with decomposition at 185—195°.

With cuprous bromide, parabromacetanilide gives a *double* salt of composition similar to the above, separating from alcohol containing hydrogen bromide, in long, colourless prisms, which suffer no loss in weight when dried in a vacuum over sulphuric acid or caustic potash.

When formanilide is added to a solution of cuprous bromide in a mixture of formic and hydrobromic acids, a salt separates at once in well-developed, doubly terminated prisms, changing, however, after a few moments into small plates consisting of the double salt of aniline

and cuprous bromide. The corresponding *salt* of formoparatoluidide crystallises in colourless, flat prisms. A. W. C.

Action of Ethereal Salts on Aromatic Amines. By STEFAN VON NIEMENTOWSKI (*Ber.*, 1897, 30, 3071—3073. Compare Hjelt, *Jahresberichte*, 1887, 1535).—Aniline reacts with ethylic acetate, yielding acetanilide and ethylic alcohol, but the reaction between ethylic acetate and aniline hydrochloride is quite different. When the salt (13 grams) is heated with ethylic acetate (9 grams) for 3 hours at 225°, the chief products are mono- and di-ethylaniline hydrochlorides and acetic acid.

The reaction appears to be a general one, aniline hydrochloride and ethylic formate yield ethylaniline hydrochloride and the decomposition products of formic acid; the amount of tertiary amine formed is usually small, even when excess of the ethereal salt is employed. J. J. S.

The Hydrochlorides of Methylaniline and Dimethylaniline. By ROLAND SCHOLL and RICHARD ESCALES (*Ber.*, 1897, 30, 3134—3137).—Methylaniline hydrochloride, which can readily be obtained crystalline by passing dry hydrogen chloride into a cooled ethereal solution of the base, deliquesces on exposure to the atmosphere, and is insoluble in ether and benzene, readily soluble in alcohol. *Dimethylaniline monhydrochloride*, $\text{NMe}_2\text{Ph}\cdot\text{HCl}$, which separates as a white, crystalline mass on passing hydrogen chloride into the cooled base, melts at about 85—95° and rapidly deliquesces on exposure to the air. When it is treated with an excess of hydrogen chloride, the *dihydrochloride*, $\text{NMe}_2\text{Ph}\cdot 2\text{HCl}$ is formed, which melts at about 60—70°, and when heated at 65—75° is reconverted into the monhydrochloride. These salts can also be obtained by passing hydrogen chloride into an ethereal solution of the base. A. H.

Reduction of Metanitrodimethylparatoluidine. By JOHANNES PINNOW (*Ber.*, 1897, 30, 3119—3122).—When metanitrodimethylparatoluidine is reduced, it not only yields the corresponding amido-compound, but also a substance containing chlorine, not yet isolated, and a solid base of high boiling point, which appears to be *metadimethylbenzimidazole*, $\text{C}_9\text{H}_{10}\text{N}_2$; the latter, which is also formed when metamidomethyltoluidine is heated with formic acid, boils at 301° (uncorr.) under a pressure of 780 mm., and crystallises in needles melting at 94·5—95·5°. The *hydrochloride*, $\text{C}_9\text{H}_{10}\text{N}_2\cdot\text{HCl}$, crystallises with H_2O in needles and, after being dried, melts at 214—215° (uncorr.); the *picrate* crystallises in minute needles, and not in plates, as previously stated (*Abstr.*, 1896, i, 161). The base is not acted on by nitrous acid and acetic anhydride, and, therefore, probably does not contain a primary or secondary amido-group.

Derivatives of benzimidazole have been obtained by the reduction of several other nitro-compounds, and the reaction is being further investigated. A. H.

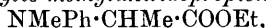
Formation of Chains. XXIV. Benzylamine. XXV. Methylaniline. XXVI. Ethylaniline. By CARL A. BISCHOFF (*Ber.*, 1897, 30, 3169—3173, 3174—3178, 3178—3180. Compare this vol., i, 73, 131).—The numbers in the following table give the approximate extent

in percentages of the theoretical maximum to which action takes place between the amines and ethylic salts there tabulated.

Ethylic salt.	Benzylamine.		Methylaniline.	Ethylaniline.	
	At 100°	At 120°	At 100°	At 100°	At 120°
Bromopropionate	98·0	99·4	91·0	78·7	95·5
Bromophenylacetate	59·5		69·1	46·5	
Bromobutyrate		94·4	65·4		66·3
Bromisobutyrate		90·0	7·7		8·0
Bromisovalerate		87·7	0·0		8·1

The following new substances were prepared in the course of the investigation.

Ethylic benzylamidopropionate, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{COOEt}$, is a colourless oil having a faint ammoniacal odour; it boils at 265—275°. *Ethylic benzylamidobutyrate*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CHEt}\cdot\text{COOEt}$, boils at 275—285°. *Ethylic benzylamidoisovalerate*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CHPr}^i\cdot\text{COOEt}$, boils at 170—175° under a pressure of 25 mm., and at 274—276° under atmospheric pressure; the first portion of the distillate consists of benzylamine carbonate. *Ethylic methylanilidopropionate*,



and *ethylic methylanilidobutyrate*, $\text{NMePh}\cdot\text{CHEt}\cdot\text{COOEt}$, are oils, and *ethyl methylanilidophenylacetate*, $\text{NMePh}\cdot\text{CHPh}\cdot\text{COOEt}$, crystallises from petroleum in needles, and melts at 72°. α -*Bromopropionylmethylanilide*, $\text{NMePh}\cdot\text{CO}\cdot\text{CHMeBr}$, separates from petroleum in triclinic crystals, and melts at 46°; α -*bromobutyrylmethylanilide*, $\text{NMePh}\cdot\text{CO}\cdot\text{CHEtBr}$, boils at 170—180° under a pressure of 10 mm. α -*Bromisobutyrylmethylanilide*, $\text{NMePh}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$, crystallises from petroleum and melts at 44°. *Ethylic ethylanilido- α -propionate*, $\text{NEtPh}\cdot\text{CHMe}\cdot\text{COOEt}$, boils at 268—270° under a pressure of 771 mm.; *Ethylic ethylanilido- α -butyrate*, $\text{NEtPh}\cdot\text{CHEt}\cdot\text{COOEt}$, boils at 273—276° under a pressure of 751 mm.

α -*Bromopropionylethylanilide*, $\text{NEtPh}\cdot\text{CO}\cdot\text{CHMeBr}$, and α -*bromobutyrylethylanilide*, $\text{NEtPh}\cdot\text{CO}\cdot\text{CHEtBr}$, are viscous oils; α -*bromisobutyrylethylanilide*, $\text{NEtPh}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$, melts at 80—80·5°. α -*Bromisovaleryl-ethylanilide*, $\text{NEtPh}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHMe}_2$, is a viscous oil, and boils at 148—165° under a pressure of 4 mm.

M. O. F.

Formation of Chains. XXIII. Orthamidophenol and Paramidophenol. By CARL A. BISCHOFF (*Ber.*, 1897, 30, 2926—2930). —Orthamidophenol reacts with ethylic α -bromopropionate in presence of sodium sulphite, which is added to prevent oxidation, producing *methylphenomorpholone*, $\text{C}_6\text{H}_4\begin{matrix} \text{NH}\cdot\text{CHMe} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{matrix}$, which crystallises in rhom-

bic tablets melting at 109—111°, whilst ethylic α -bromobutyrate, under the same conditions, undergoes a different type of reaction, yielding *ethylic orthohydroxyanilidobutyrate*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHEt}\cdot\text{COOEt}$, which melts at 81°. Ethylic α -bromisobutyrate reacts differently from either of the preceding, and forms *isobutyro-orthamidophenol*

[*orthamidophenylic isobutyrate*], $\text{CHMe}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, which crystallises in asymmetric tablets and prisms melting at $112-115^\circ$.

Paramidophenol, on the other hand, only forms derivatives of a single type with these three brominated acids. *Ethylic parahydroxy-anilidopropionic acid*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CHMe} \cdot \text{COOEt}$, formed from ethylic α -bromopropionate, melts at 86° ; *ethylic parahydroxyanilidobutyrate* crystallises in colourless, lustrous needles, melting at 59.5° , whilst *ethylic parahydroxyanilido-isobutyrate*, which is apparently formed in two isomeric modifications, only one of which has been isolated, crystallises in lustrous, yellowish prisms melting at $91-91.5^\circ$. The isobutyric derivative is formed in the smallest quantity.

A. H.

Action of Formaldehyde on Paraphenetidine and on Paranisidine in Acid Solution. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, 21, 395—396).—When paraphenetidine is treated with an excess of formaldehyde in the presence of strong hydrochloric acid, a *hydrochloride* is obtained which, on treatment with alkali, yields a *base*, $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$, crystallising from alcohol in glistening plates and melting at 140° ; it is practically insoluble in water and only sparingly soluble in ether. It yields two *hydrochlorides*, $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2 \cdot 2\text{HCl}$, melting at 122° , and $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2 \cdot \text{HCl}$, melting at 193° . The *salicylate* of the base has physiological properties similar to those of cocaine.

Paranisidine, when treated in the same manner, yields two isomeric *bases*, $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_2$. The one is more readily soluble in alcohol, crystallises in glistening plates melting at 122° , is but sparingly soluble in ether, and its *hydrochloride* melts at 210° . The second is sparingly soluble in alcohol, melts at 170° , and yields a *hydrochloride* melting at 112° .

J. J. S.

Derivatives of Tetramethylmetaphenylenediamine. By JOHANNES PINNOW and M. WEGNER (*Ber.*, 1897, 30, 3110—3119).—Tetramethylmetaphenylenediamine is best prepared by the action of hydrobromic acid and methylic alcohol on phenylenediamine. *Amido-tetramethylmetaphenylenediamine*, prepared by reducing the nitroso-tetramethylmetaphenylenediamine described by Witt (*Abstr.*, 1885, 782), is a colourless liquid which boils at 209.4° under a pressure of 112 mm., has a sp. gr. = 1.0203 at $22^\circ/4^\circ$, and rapidly becomes dark coloured on exposure to the air. The *hydrochloride*, $\text{C}_{10}\text{H}_{17}\text{N}_3 \cdot 2\text{HCl}$, melts at 164° (uncorr.), the *hydrobromide* at 179° (uncorr.), and the *hydriodide* at 175° (uncorr.); of the remaining salts may be mentioned the *sulphate*, which readily deliquesces, the *stannochloride*, which melts at 171° , and the *picrate*, which crystallises in small, feathery prisms and melts at 169° (uncorr.). The *acetyl* derivative crystallises in lustrous tablets, which melt at 85° , whereas the *benzoyl* derivative has not been obtained in the crystalline state, although it yields a crystalline *picrate* melting at 128° (uncorr.). *Tetramethyldiamidophenyl-carbamide* forms small, microscopic needles, which melt at 173° (uncorr.). *Asymmetrical tetramethyldiamidocarbaniide* crystallises in lustrous prisms melting at 175° (uncorr.), whilst the corresponding *thiocarbaniide* forms compact crystals melting at 143° (uncorr.). *Tetramethyldiamidourethane* has not been obtained in the crystalline state, but it yields a

picrate, which crystallises in light yellow plates and melts at 167° (uncorr.). *Tetramethylldiamidobenzenesulphanilide*, $C_{16}H_{21}N_3SO_2$, crystallises in prisms melting at 84° and decomposes when boiled with water.

Acetic anhydride converts tetramethyltriamidobenzene into a crystalline compound which was only obtained in very small quantity and appears to be a benzimidazole derivative. *Tetramethylmetaphenylenediamineazobenzenesulphonic acid* is a brownish-red mass which melts at 189° (uncorr.), and on reduction yields the tetramethyltriamidobenzene described above. The constitution of the triamido-base is shown by the fact that, on methylation, it is converted into the same hexamethyltriamidobenzene as is given by dimethyldiamido-aniline, the constitution of which is already known. The *hexamethyl* compound boils at 184° (corr.) under a pressure of 40 mm., and yields a crystalline *methiodide*, $C_6H_3N_3Me_6 \cdot 3MeI + 2MeOH$, crystallising in needles, which melt and decompose at 164.5° (uncorr.). α -Diamidodimethylaniline boils at 195.5° (corr.) under a pressure of 40 mm. and yields a *hydrochloride* which melts at 225° (uncorr.), the corresponding hydrobromide melting at 207° (uncorr.) and the hydriodide at 190° (uncorr.). *Dinitrotetramethylmetaphenylenediamine* is formed when the tetramethyl compound is submitted to nitration by the method previously employed for dimethylaniline (Abstr., 1896, i, 427).

A. H.

Acylimido-ethers. By HENRY L. WHEELER, PERCY T. WALDEN and H. F. METCALF (*Amer. Chem. J.*, 1898, 20, 64—76. Compare Abstr., 1897, i, 280).—The preparation of acylimido-ethers in an approximately pure state is in some cases attended with difficulty on account of the ease with which they react with water, in presence of acids, in one of two ways; either alcohol is separated and a diacylamide formed, or a monacylamide and an ethereal salt are produced. To what extent the acylimido-ethers decompose in the first case otherwise than indicated has not been fully investigated, but when acted on with ammonia they give acylamidines, which will form the subject matter of another paper. The imido-ether hydrochlorides were obtained by Pinner's well known method, and the free ethers were prepared according to Bushong's directions (Abstr., 1896, i, 546).

Benzimidomethylic ether, $OMe \cdot CPh : NH$, boils at 96° under a pressure of 13 mm., and on standing deposits crystals of cyanophenine. The *picrate* forms heavy, lemon-yellow crystals melting at 163° .

Benzobenzimidomethylic ether, $OMe \cdot CPh : NBz$, prepared by the action of benzoic chloride on the above imido-ether, is a colourless oil boiling at 210 — 212° (12 mm.); when treated with a little hydrochloric acid in alcoholic solution, dibenzamide is formed.

Carbethoxybenzimidomethylic ether, $OMe \cdot CPh : N \cdot COOEt$, obtained by the action of ethylic chlorocarbonate on benzimidomethylic ether, is a colourless oil boiling at 155° (14 mm.); hydrochloric acid converts it into benzoylurethane.

Ethyloxalybenzimidomethylic ether, $OMe \cdot CPh : N \cdot CO \cdot COOEt$, obtained from the above imido-ether and ethylic chloroxalate boils at 192° (14 mm.). On standing, or when boiled with water, it is converted into ethylic benzoate and oxamethane, and is decomposed by aqueous

ammonia into oxamide and methylic benzoate. The corresponding *ethyl ether* boils at 190—195° (11 mm.).

Benzimidoethylic ether distils at 101—102° (15 mm.); when treated with mercuric chloride in alcoholic solution, an additive product separates in colourless needles.

Acetobenzimidethylic ether boils at 156° (17 mm.); when mixed with benzoic chloride and kept at 100—120°, tribenzamide separates. The corresponding *propionyl* compound is an oil boiling at 161—162° (17 mm.); when treated with hydrochloric acid, it is converted into *propionobenzamide*, which crystallises in needles or prisms and melts at 98°. The normal *butyryl* compound boils at 167° (16 mm.) and when treated in a similar manner yields *butyrobenzamide* in beautiful colourless prisms melting at 104—105°. The *benzoyl* compound, which separates in rhomboidal crystals melting at 65°, is converted by sulphuric acid into dibenzamide, whilst the action of benzoic chloride yields tribenzamide; as the latter reaction is analogous to that of the acyl chlorides on the isoanilides, in which case diacylanilides are formed, it indicates that in triacylamides all three acyl groups are attached to nitrogen.

Dibenzoethylamide, NEtBz_2 , isomeric with benzobenzimidethylic ether, is obtained by treating the sodium salt of ethylbenzamide with benzoic anhydride; it crystallises from alcohol in colourless prisms melting at 101—102°.

Benzimidopropylic ether is a colourless, pleasant smelling oil boiling at 232° under ordinary atmospheric pressure, or at 115.5° (12 mm.). The *hydrochloride* melts at 125°, giving off ethylic chloride and forming benzamide; the *picrate* crystallises in lemon-yellow prisms melting and decomposing at 261°.

Acetobenzimidopropylic ether, obtained by the action of acetic chloride on the imido-ether, is an oil boiling at 153° (13 mm.); on exposure to air it deposits acetobenzamide. The corresponding *benzoyl* compound boils at 231—232.5° (17 mm.) and gives dibenzamide on treatment with hydrochloric acid.

Benzimidoisobutylic ether boils without decomposition at 248—250° under atmospheric pressure, or at 117.5—120° (9 mm.).

Benzoylbenzimidoisobutylic ether melts at 54.5° and boils at 228—235° (15 mm.).

Phenylacetimidomethylic ether, $\text{OMe}\cdot\text{C}(\text{C}_7\text{H}_7):\text{NH}$, is a pleasant smelling oil distilling at 114.5—115° (20 mm.). The *ethylic ether* boils at 116° (15 mm.).

Benzoylphenylacetimidoethylic ether, $\text{OEt}\cdot\text{C}(\text{C}_7\text{H}_7):\text{NBz}$, boils at 215—216° (13 mm.) and readily decomposes into benzamide and phenylethylic acetate.

A. W. C.

Influence of the Side Chain on the Velocity of Decomposition of Benzene Derivatives. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1897, 30, 2966—2975).—*Disubstituted benzene derivatives*.—The reaction between allylic bromide and the three toluidines has been studied and the following velocity constants obtained: ortho-toluidine, 54; meta-, 445, and para-, 96.

The action of dipropylamine on the three bromonitrobenzenes was

studied by heating the two substances together, without any solvent, for 45 minutes in nitrobenzene vapour. The numbers are: ortho-bromonitrobenzene, 88.8; meta-, 0, and para-, 21.7 per cent.

The author regards these as two phases of the same type of distribution of velocity constants, both of which are characterised by the preponderating influence of the meta side chain. In the first case, when the meta-position gives a maximum, the ortho gives a minimum, and in the second, when the meta gives a minimum, the ortho gives a maximum; in both, the para takes an intermediate position. The second type of distribution is met with in the action of allylic bromide on chloranilines, and also in the hydrolysis of the three tolylsuccinimides by sodium hydroxide at 25° (Miolatti and Lotti). The constants are, for the chloranilines, ortho, 9; meta, 23; para, 34; and for the tolylsuccinimides, ortho, 8558; meta, 10980; para, 1200. In both, the ortho-compound coincides with a minimum constant, and the para with a maximum, the meta being intermediate. The second phase of this second type, namely, where the para-position corresponds with a minimum and the ortho with a maximum, has not been met with as yet in any chemical reaction. The dissociation constants of the chloro- and hydroxy-benzoic acids (compare Ostwald) follow, however, the above order; in both cases, the constant for the ortho-acid is a maximum and for the para-, a minimum.

Tri-derivatives of Benzene.—Similar types are to be met with here, if we suppose that two of the three groups remain fixed and the third alone changes its position. For example, in the hydrolysis of the six xylylsuccinimides with sodium hydroxide, Miolatti and Lotti give the following constants: ortho-ortho, 1571; ortho-meta, 8147; ortho-para, 8653; meta-ortho, 8757; meta-meta, 11450; meta-para, 12700. In both sets, we have the first phase of the second type, namely, a maximum with the para-compound and a minimum with the ortho-.

In the action of allylic bromide on the six xylydines, the following numbers were obtained, $[Me_2:NH_2 = 1:3:2]$ 129, $[1:2:3]$ 400, $[1:3:4]$ 235; $[1:4:3]$ 185, $[1:3:5]$ 209, $[1:2:4]$ 707. In both these sets we find a minimum in the ortho-position, but in the first set the maximum corresponds with the meta-, and in the second with the para-position.

Tetra-derivatives.—The action of allylic bromide on mesidine and cumidine gave the constant for mesidine=115, and for cumidine=174.

The author compares these results with the rules of orientation found by Körner, Griess, and others, when benzene and its derivatives are nitrated, chlorinated, &c. It is thought that all these results can only be explained by the adoption of both the diagonal and the Kekulé formula for benzene.

J. J. S.

Action of Diazomethane on Nitrosobenzene. By HANS VON PECHMANN (*Ber.*, 1897, 30, 2871—2879. Compare this vol., i, 75).—Further evidence is adduced in favour of regarding the compound obtained from diazomethane and nitrosobenzene as the *n*-phenyl ether of glyoxime. The substance is synthesised from formaldehyde and phenylhydroxylamine with the intermediate production of the com-

pound, $\text{CH}_2(\text{NPh}\cdot\text{OH})_2$; it is also obtained from glyoxal and phenylhydroxylamine, and is resolved into these products under the influence of acids and of phenylhydrazine. Acetic anhydride converts it first into oxanilide, and subsequently into vinylidene oxanilide (this vol., i, 135).

Glyoxime *n*-phenyl ether is prepared by treating an ice-cold solution of nitrosobenzene (5 grams) in ether, with an ethereal solution of diazomethane obtained from nitrosomethylmethane (5 grams); the mother liquor of the first crop of crystals deposits a second fraction when concentrated and treated with petroleum, and the filtrate from this fraction contains phenylhydroxylamine and azoxybenzene. The most convenient method of preparation consists in treating a solution of phenylhydroxylamine with the hydrogen sodium sulphite compound of glyoxal, and acidifying the solution with acetic acid.

Glyoxime *n*-*parabromophenyl* ether is prepared from diazomethane and nitrosobromobenzene, and also by brominating the phenyl ether; it crystallises from hot, glacial acetic acid in yellow needles, and melts at 278° . Alcoholic potash converts it into *paradibromazoxybenzene*, which crystallises from alcohol in yellow leaflets, and melts at 172° .

Glyoxime *n*-phenyl ether is resolved into phenylhydroxylamine and glyoxal by phenylhydrazine, *parabromophenylhydrazine*, and asymmetric methylphenylhydrazine, which give rise to the respective osazones. Alcoholic potash converts it into azoxybenzene and aniline.

M. O. F.

Reduction Products of the Nitrated Dimethylanilines. By EMILIO NOELTING and ÉMILE FOURNEAUX (*Ber.*, 1897, 30, 2930—2947).—*Metanitrodimethylaniline hydrochloride*, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2\cdot\text{HCl}$, crystallises in colourless needles which are sparingly soluble in alcohol, the *hydrogen sulphate* in colourless plates, and the *picrate* in small, greenish-yellow needles.

Various products are obtained by the reduction of metanitrodimethylaniline, according to the reducing agent employed. *Metazoxydimethylaniline*, $\text{O} \begin{array}{c} \text{N}\cdot\text{C}_6\text{H}_3\cdot\text{NMe}_2 \\ | \\ \text{N}\cdot\text{C}_6\text{H}_3\cdot\text{NMe}_2 \end{array}$, formed by heating the nitro-compound with a concentrated solution of sodium methoxide in methylic alcohol, forms compact, orange-red crystals melting at $88\text{--}89^\circ$, and yields colourless, soluble salts with acids; of these, the *hydrochloride* crystallises in small, white needles, the *hydrogen sulphate* in colourless needles, and the *oxalate* in pale yellow needles; the *platinochloride* is a yellow, crystalline precipitate; the *picrate* crystallises in lustrous, red, pointed pyramids, and the *ferrocyanide* in pale yellow needles almost insoluble in water. The azoxy-compound is identical with that produced by the methylation of the metazoxyaniline, formed by the action of aqueous soda and zinc dust on nitraniline, and also with the hydrazoaniline described by Haarhaus (*Annalen*, 135, 164). When its hydrobromide is boiled with methylic alcohol, or when the azoxy-compound itself is treated with methylic iodide in presence of an alkali, metazoxydimethylaniline is produced.

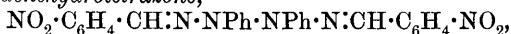
Metazoxydimethylaniline methiodide forms small, yellow crystals which melt and decompose at 190° .

Metazodimethylaniline, $N_2(C_6H_3 \cdot NMe_2)_2$, which has previously been described by Lauth (Abstr., 1892, 1222) is best prepared by reducing the nitro-derivative with zinc dust and aqueous soda, and then reoxidising the hydrazo-derivative thus formed. It crystallises in red needles melting at 118° , and, with acids, yields coloured, sparingly soluble salts; of these, the *hydrochloride* crystallises in golden-yellow plates, and the *platinochloride* is an orange-coloured, crystalline powder; the *sulphate*, *oxalate*, *picrate*, and *ferrocyanide* are all yellow, crystalline substances. Metazodimethylaniline is also formed by the methylation of metazoaniline. The *methiodide* forms orange-yellow crystals which melt and decompose at 230° ; the corresponding ammonium hydroxide, like that of the azoxy-derivative, is very unstable. *Metazoaniline*, obtained in the preparation of metazoxyaniline, crystallises in orange-yellow needles melting at 144° , and is identical with the compound described by Graeff (Abstr., 1885, 1127) as hydrazoaniline. The *hydrobromide* crystallises in plates which are readily soluble in water. *Metahydrazodimethylaniline*, $N_2H_2(C_6H_3 \cdot NMe_2)_2$, crystallises in white needles melting at $99-100^\circ$, and oxidises very readily when moist. Tetramethyldiamidobenzidine, which has also been described by Lauth, can be obtained by the reduction of metazodimethylaniline with tin and alcoholic hydrogen chloride, or by the direct action of hydrochloric acid on the hydrazo-compound; it crystallises in colourless needles melting at $166.5-166^\circ$. An acid solution of the base gives an intense violet coloration with a nitrite. The *hydrochloride*, *sulphate*, and *oxalate* are all colourless, crystalline substances. The benzidine is accompanied by dimethylmetaphenylenediamine and a diphenylene derivative, the *hydrochloride* of which, $C_{16}H_{12}N_4 \cdot 4HCl + 4H_2O$, crystallises in colourless needles. *Tetramethyldiamidobenzidine methiodide* crystallises in colourless needles, and yields a stable ammonium hydroxide. The benzidine compound is converted by methylation into the methiodide of *octomethyldiamidobenzidine*; the *dimethiodide* of this, $C_{12}H_6(NMe_2)_4 \cdot 2MeI$, crystallises in long, colourless needles which melt and decompose at 190° ; the *tetramethiodide* forms lustrous, white needles, and melts and decomposes at 205° . The free base, which has only been obtained in very small quantity, crystallises in needles melting at $176-178^\circ$. Tetramethyldiamidobenzidine readily forms colouring matters with diazo-salts, &c. *Monophenylazotetramethyldiamidobenzidine* forms orange-coloured needles melting at $220-221^\circ$, and dyes brown on a tannin mordant. *Diphenyl-disazotetramethyldiamidobenzidine* is similar to the foregoing, but dyes a redder shade on tannin; the *platinochloride* forms reddish-brown crystals. The colouring matters formed with diazobenzenesulphonic acid are less powerful dyes; with nitrosodimethylaniline hydrochloride an indamine is formed; an azine has also been prepared which dyes cotton directly a bright bluish-violet. The colouring matters obtained from the isomeric diphenylene compound are similar in general character to the foregoing; the azines do not, however, dye unmordanted cotton.

Parazodimethylaniline, which is obtained in small amount by the reduction of the corresponding azoxy-compound, is identical with the compound obtained by the action of phenylhydrazine on nitrosodimethylaniline by O. Fischer and Wacker (Abstr., 1888, 1286). The authors were unable to obtain the compound described by Barbier and

Vignon (Abstr., 1888, 54) as being formed by heating an alcoholic solution of aniline and nitrosodimethylaniline. A. H.

Isomerism amongst the Oxidation Products of the Hydrazones. By GAETANO MINUNNI (*Gazzetta*, 1897, 27, ii, 215—235).—On oxidising metanitrobenzylidenephénylhydrazone suspended in ether by boiling it with amylic nitrite, a mixture of dimetanitrobenzylidenediphenylhydrotetrazone and dehydrometanitrobenzylidenephénylhydrazone crystallises out and is separated mechanically. *Diphenyldimetanitrobenzylidenehydrotetrazone*,



which crystallises in thin, yellow needles, partially melts at 147—148° and then resolidifies, being converted into isodehydrometanitrobenzylidenephénylhydrazone; it is only sparingly soluble in cold acetic acid, alcohol or benzene, but soluble in chloroform, and turns blue with concentrated sulphuric acid. The isomeric *dehydrophenylmetanitrobenzylidenehydrazone*, $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_4$, crystallises in minute, yellow needles, melting at 190—194°, and is sparingly soluble in alcohol, acetic acid, or chloroform. On heating the tetrazone to 154°, it changes into *isodehydrophenylmetanitrobenzylidenehydrazone*, $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_4$, a yellow crystalline powder which melts at 244—245° without blackening, whereas the dehydro-compound blackens at that temperature; unlike its two isomerides, it gives no blue colour with concentrated sulphuric acid.

Phenylanisylidenehydrazone, when similarly oxidised with amylic nitrite, yields a mixture of diphenyldianisylidenehydrotetrazone and dehydrophenylanisylidenehydrazone, which may be separated by crystallisation from benzene and alcohol. *Diphenyldianisylidenehydrotetrazone*, $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_6$, crystallises in yellow needles melting at 152°, and is also obtained in small yield by treating an ethereal solution of anisylidenephénylhydrazone with yellow mercuric oxide; the isomeric *dehydroanisylidenephénylhydrazone*, which melts at 190°, is yellow and crystalline, and is also obtained by heating the tetrazone at 155°.

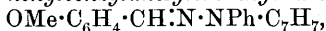
Phenylcuminyldienehydrazone, when oxidised with amylic nitrite, yields a mixture of dicuminyldenediphenylhydrotetrazone and dehydrocuminyldienephénylhydrazone which can be separated by crystallisation from ether and alcohol. *Diphenylcuminyldenedihydrotetrazone*, $\text{N}_2\text{Ph}_2(\text{N} : \text{CH} \cdot \text{C}_6\text{H}_4\text{Pr})_2$, crystallises in flattened, canary-yellow needles sparingly soluble in organic solvents; melting points were observed varying between 156° and 160°; this is due to its conversion into isodehydrophenylcuminyldienehydrazone, described below. *Dehydrophenylcuminyldienehydrazone*, $\text{C}_{32}\text{H}_{34}\text{N}_4$, is a crystalline, yellow powder melting at 151.5—152°, and dissolves readily in cold benzene or chloroform. On heating diphenyldicuminyldienehydrotetrazone to 165° and immediately cooling, it is converted into the isomeric *isodehydrophenylcuminyldienehydrazone*; this is a white, crystalline powder melting at 215—219°, very soluble in cold chloroform, and giving a reddish coloration with concentrated sulphuric acid, differing in this respect from its two isomerides which give a blue under similar conditions.

Phenylfurfuryldienehydrazone, on oxidation with amylic nitrite,

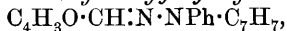
yields a mixture of diphenyldifurfurylidenehydrotetrazone and dehydrofurfurylidenephenylhydrazine, which can be separated by crystallisation from benzene. *Diphenyldifurfurylidenedihydrotetrazone*, $N_2Ph_2(N:CH \cdot C_4OH_3)_2$, crystallises in microscopic, yellow needles melting at $135-136^\circ$ with decomposition; no isomeride could be isolated from the substance after fusion. *Dehydrophenyldifurfurylidenehydrazone*, $C_{22}H_{18}N_4O_2$, crystallises in colourless needles melting at $155.5-161^\circ$; neither isomeride gives a characteristic colour with concentrated sulphuric acid. W. J. P.

Derivatives of α -Phenylbenzylhydrazine. By GAETANO MINUNNI. (*Gazzetta*, 1897, 27, ii, 235-244).— α -Phenylbenzylhydrazine combines readily with aldehydes; the hydrochloride of the hydrazine (1 mol.) and sodium acetate (1 mol.) are dissolved in alcohol, mixed, the sodium chloride filtered off, and the aldehyde (1 mol.) added to the filtrate. The following hydrazones were prepared in this way.

Phenylbenzylcuminyldenehydrazone, $C_6H_4Pr \cdot CH:N \cdot NPh \cdot C_7H_7$, crystallises in white needles melting at $89-90^\circ$, and dissolves readily in organic solvents. *Phenylbenzylanisilydenehydrazone*,



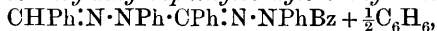
crystallises in yellowish needles melting at $135-136^\circ$. *Phenylbenzyl-metanitrobenzylidenehydrazone* crystallises in beautiful, yellow needles melting at $140-141^\circ$. *Phenylbenzylfurfurylidenehydrazone*,



separates in small, yellow crystals melting at 138° . *Phenylbenzyl-orthohydroxybenzylidenehydrazone* crystallises in white needles melting at 117.5° , and when boiled with acetic anhydride yields *phenylbenzyl-orthoacetoxybenzylidenehydrazone*, which crystallises in long, white needles melting at $141.5-142^\circ$.

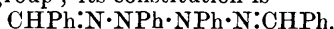
Benzonitrile and α -phenylbenzylhydrazine do not react in benzene solution in presence of sodium, neither is a semicarbazide obtained on heating carbamide with α -phenylbenzylhydrazine at $165-170^\circ$, but instead a substance of the composition $C_{39}H_{34}N_4$, crystallising in nearly white needles melting at $108-109^\circ$; the study of this substance is being continued. W. J. P.

Constitution of Dehydrophenylbenzylidenehydrazone and its Conversion into Dibenzylidenediphenylhydrotetrazone. By GAETANO MINUNNI (*Gazzetta*, 1897, 27, ii, 244-262).—On heating dehydrophenylbenzylidenehydrazone with benzoic chloride for an hour on the water bath, pouring into water, and adding much potassium carbonate, *monobenzoyldehydrophenylbenzylidenehydrazone*,



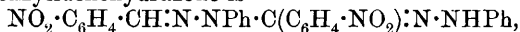
separates, and when crystallised from benzene is obtained as a crystalline powder melting at $172-173.5^\circ$; the benzene is but slowly evolved at $120-125^\circ$. On crystallising this substance from boiling alcohol, it is converted into an *isomeride*, $C_{26}H_{21}N_4Bz$, which crystallises in white needles melting at $187-188^\circ$ with decomposition; both isomerides are hydrolysed by alcoholic potash with formation of benzoic acid and dehydrophenylbenzylidenehydrazone. The cause of the isomerism is unexplained. Dehydrophenylbenzylidenehydrazone yields an *acetyl* derivative, $C_{26}H_{21}N_4Ac$, which crystallises in colourless,

lustrous prisms melting at $124-125.5^\circ$, and is hydrolysed by alcoholic potash, yielding acetic acid and dehydrophenylbenzylidenetetrazone. The latter, therefore, contains one, and only one, imido-group, and has the constitution assigned to it above. Diphenyldibenzylidenetetrazone gives no acetyl or benzoyl derivative, and consequently contains no imidogen group; its constitution is

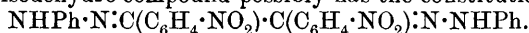


Dehydrophenylbenzylidenetetrazone should yield a nitroso-compound if the constitution assigned above be correct; on treating it, in acetic acid and chloroform solution, with sodium nitrite and hydrochloric acid, the *nitroso*-compound could not be isolated in a pure state, but diphenyldibenzylidenetetrazone was separated. The hydrazone and the tetrazone are thus mutually convertible.

On the basis of these results, constitutions can be assigned to the substances described in the last abstract but one. Thus, diphenyldimetanitrobenzylidenetetrazone melting at 148° has the constitution $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{NPh}\cdot\text{NPh:N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, dehydrophenylmetanitrobenzylidenetetrazone is

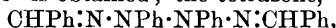


whilst the isodehydro-compound possibly has the constitution

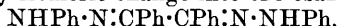


W. J. P.

Action of Acid Chlorides on the Hydrotetrazones. By GAETANO MINUNNI (*Gazzetta*, 1897, 27, ii, 277—292).—In the preceding abstracts, the author has shown that diphenyldibenzylidenetetrazone gives no acidic derivative with acetic anhydride or benzoic chloride. On mixing the tetrazone with benzoic chloride, heating to 90° , cooling and treating with alcohol, the isomeric benzil- β -osazone melting at $221-223^\circ$ is obtained; the tetrazone,



is thus converted by isomeric change into the osazone,



On distilling the osazone prepared either from the tetrazone or from benzil with benzoic chloride, the same triphenylosotriazone, $\text{C}_{20}\text{H}_{15}\text{N}_3$, melting at $120-121^\circ$ is obtained. The tetrazone and the osazone react with benzoic chloride in a boiling salt water bath with production of a *substance* of the composition $(\text{C}_{14}\text{H}_{10}\text{N})_x$, which crystallises in white scales melting at $211.5-212.5^\circ$. At $95-97^\circ$, the tetrazone gives with benzoic chloride a *substance* of the composition $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_3$; it is a white powder melting at $183-187^\circ$.

The product of the action of benzoic chloride on the tetrazone at $90-95^\circ$, contains, besides benzil- β -osazone and the substance melting at $183-187^\circ$, a third compound, $\text{C}_{42}\text{H}_{34}\text{N}_4\text{O}_4$, which crystallises in white needles melting at $165-168^\circ$.

W. J. P.

Oxidation of Formazyl Compounds derived from Acetyl, Benzoyl, and Methane. By EDGAR WEDEKIND (*Ber.*, 1897, 30, 2993—2999).—It has been shown already (von Pechmann and Runge, *Abstr.*, 1894, i, 240) that formazyl derivatives, $\text{NPh:N}\cdot\text{CR:N}\cdot\text{NPh}$, yield tetrazolium bases, $\text{CR}\leq\begin{smallmatrix} \text{N:NPh}\cdot\text{OH} \\ \text{N}\cdot\text{NPh} \end{smallmatrix}$, on oxidation. Some further

instances of this are now described. The method of oxidation adopted was to dissolve the formazyl compound in chloroform (or alcohol), add alcoholic hydrochloric acid, and pass in nitrous anhydride, when the chloride of the tetrazolium base, $\text{CN}_4\text{RPh}_2\text{Cl}$, separates.

Formazylic cyanide ($\text{R} = \text{CN}$; von Rothenburg, Abstr., 1894, i, 273) yields colourless *cyanodiphenyltetrazolium chloride*; this melts at $265\text{--}267^\circ$, is perhaps hydrolysed by hydrochloric acid to the carboxylic acid, and is reduced to formazylic cyanide by alkaline stannous chloride solution, and also by alkalis. Attempts were made to prepare formazylic bromide and chloride by the action of ethylic brom- and chlor-acetates on diazobenzene chloride in alkaline solution, but the products were found to contain no halogen; they were respectively yellowish-brown and dark-coloured powders, and melted at $198\text{--}200^\circ$ and $177\text{--}178^\circ$. Formazyl methyl ketone (acetyl formazyl; $\text{R} = \text{Ac}$; Bamberger, Abstr., 1893, i, 159) is oxidised to *methylketodiphenyltetrazolium*, which could only be isolated in the form of its yellowish-white *platinochloride*; this melts and decomposes at 239° . The yield in this case is only about half of the theoretical. An impure *phenylhydrazone* of the *chloride*, decomposing at $112\text{--}115^\circ$, was also obtained. Formazyl phenyl ketone (benzoylformazyl; $\text{R} = \text{Bz}$; Bamberger and Witter, Abstr., 1894, i, 98) is oxidised to *phenylketodiphenyltetrazolium*, of which the yellowish-white *chloride* melts at $220\text{--}225^\circ$, and forms a reddish-brown *phenylhydrazone* melting and decomposing at $104\text{--}108^\circ$.

Formazylmethane (methylformazyl; $\text{R} = \text{Me}$; Bamberger and Müller, Abstr., 1894, i, 183) is not oxidised to a tetrazolium base when treated in the manner described; the product is orange coloured, melts at 232° , and contains chlorine, but it has not the properties of the salt of a base. C. F. B.

Bismarck-brown. By ERNST TÄUBER and FRANZ WALDER (*Ber.*, 1897, 30, 2899—2902. Compare this vol., i, 23).—In a dissertation published in 1895, Küchle expressed the view that triamidoazobenzene is but an inconsiderable constituent of Bismarck-brown, claiming on somewhat slender evidence that the colouring matter consists chiefly of phenylenedisazometaphenylenediamine. The authors find that this view is correct, comparison of the latter substance synthesised from diazotised metaphenylenediamine with the disazo-compound isolated from Bismarck-brown (*loc. cit.*) showing them to be identical.

Phenylenemetadisazometaphenylenediamine is prepared by slowly adding a solution of metabisdiazobenzene chloride to an ice-cold, aqueous solution of metaphenylenediamine and sodium carbonate which is well stirred; it separates from benzene in brownish-yellow crystals melting at 118° , and when recrystallised from a mixture of phenol and benzene melts at 136° .

Phenylenemetadisazometaphenylenediamine, is therefore, the chief constituent of Bismarck-brown, which contains also a small quantity of triamidoazobenzene, and a base which is insoluble in benzene.

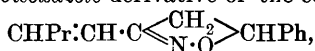
M. O. F.

Absorption of the Violet Rays of Light by Unsaturated Ketones. By OTTO WALLACH (*Chem. Centr.*, 1897, i, 373—374; from *Nachr. der Kön. Gesell. Wiss. Göttingen*, 1896, Heft 4, 1—5).—The author has previously shown (compare *ibid.*, 1896, 73) that several ketones of the terpene series absorb light of certain wave-lengths; thus pulegone and eucarvone absorb the violet rays, whilst the isomeric ketones dihydrocarvone and carvone, transmit them unabsorbed. He now finds that several unsaturated ketonic compounds, such as mesityl oxide, phorone, and mono- and di-benzylideneacetone, also strongly absorb the violet rays; he draws the conclusion that the introduction of an ethylenic linking, adjacent to a carbonyl group, produces a greater absorptive power in a derivative than that possessed by its parent substance. If the carbon atoms on *both* sides of the carbonyl group are attached to the rest of the molecule by ethylenoid linkings, a still greater absorptive power is exhibited. Thus mesityl oxide shows a greater absorption of the violet rays than acetone; and phorone a greater absorption than mesityl oxide. The same holds in the case of acetone and the mono- and di-benzylideneacetones.

Substances which absorb the violet rays must appear yellow. A series of examples is adduced to show that compounds which contain the group $\text{:C}\cdot\text{CO}\cdot\text{C}$ are yellow, and that those which contain the group $\text{:C}\cdot\text{CO}\cdot\text{C:}$ are still more yellow; for instance, the condensation products of acetone and piperonal, $\text{CH}_3\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH:CH}\cdot\text{CO}\cdot\text{CH}_3$, and $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH:CH}\cdot\text{CO}\cdot\text{CH:CH}\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\text{O}_2$; styryloacetic acid; and styrylformic acid. From the cyclic ketones containing the groups $\text{CH}_2\cdot\text{CO}$ or $\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2$, yellow derivatives are obtained by replacing the two hydrogen atoms contained in either of these groups by a doubly-linked carbon atom (compare Abstr., 1896, i, 572). The groups, $\text{C:CH}\cdot\text{CO}$ and $\text{C:CH}\cdot\text{CO}\cdot\text{CH:C}$, are therefore chromophorous (compare Kesselkaul and Kostanecki, Abstr., 1896, i, 606; Friedländer and Löwy, Abstr., 1897, i, 32). Since isothujone and carvenone transmit the violet rays, they probably do not contain the group $\text{C:CH}\cdot\text{CO}$; whilst eucarvone probably contains it.

W. A. D.

Compounds formed by the action of Hydroxylamine on Ketones of the Type $\text{CHR:CH}\cdot\text{CO}\cdot\text{CH:CHR}$. By GAETANO MINUNNI (*Gazzetta*, 1897, 27, ii, 263—276).—On leaving a mixture of dibenzylideneacetone with hydroxylamine hydrochloride, suspended in alcohol at the ordinary temperature for 10 days, a *compound* is formed which crystallises in minute, white needles, melts at $142\text{--}144^\circ$, and seems to be a *dihydroisoxazole* derivative of the constitution



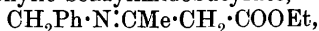
formed by intramolecular change of the oxime. The aqueous mother liquors contain small quantities of a *substance* melting at $164\text{--}165^\circ$ which is very unstable, is soluble in alkalis, and is probably the oxime of dibenzylideneacetone.

On heating hydroxylamine acetate with dibenzylideneacetone in alcoholic solution and allowing the solution to evaporate spontaneously, the compound melting at 142° is obtained together with a *substance* of

the composition $C_{17}H_{13}N_2O_2$, which crystallises in beautiful, white prisms melting at $200\cdot5$ — 202° ; it is probably formed by the interaction of the oxime with hydroxylamine.

On heating difurfurylideneacetone, hydroxylaminehydrochloride, and sodium acetate in alcoholic solution, filtering, and allowing the filtrate to evaporate spontaneously, a substance is obtained which crystallises in tufts of small prisms, melts at 162 — 164° , and has the composition $(C_4H_3O\cdot CH\cdot CH_2)_2C\cdot NOH, NH_2\cdot OH$; it seems to be an additive compound of the oxime with hydroxylamine. W. J. P.

Isomerism of Anils and Hydrazones. By ARTHUR R. HANTZSCH and ERNST VON HORNBOSTEL (*Ber.*, 1897, 30, 3003—3009).—Möhlau and Hornbostel (*Abstr.*, 1895, i, 140) have obtained two isomeric and interconvertible condensation products of ethylic acetoacetate with benzylamine. These may be regarded (1) as structurally isomeric, being respectively ethylic benzylimidobutyrate,



and benzylamidocrotonate, $CH_2Ph\cdot NH\cdot CMe\cdot CH\cdot COOEt$; (2) as stereoisomeric ethylene derivatives, being the *cis* and *trans* forms of the second of these two substances; (3) as stereoisomeric nitrogen derivatives, being the *syn* and *anti* forms of the first substance. The authors have searched for similar cases of isomerism, but with only partial success; neither with ethylic benzoylacetate, acetophenone, benzophenone, benzophenone chloride, CPh_2Cl_2 , nor anisyl phenyl ketone chloride can benzylamine be said with certainty to yield more than one condensation product. With ethylic acetoacetate, however, diphenylhydrazine does yield two interconvertible condensation products, although again with ethylic benzoylacetate only one product is obtained. If the second view of the condensation with benzylamine be adopted, then these two isomeric diphenylhydrazine derivatives must be regarded as hydrazides ($NPh_2\cdot NH\cdot CMe\cdot CH\cdot COOEt$); it is probable, however, that they are hydrazones ($NPh_2\cdot N\cdot CMe\cdot CH_2\cdot COOEt$), and if so that view must be rejected. The authors prefer to adopt the third view provisionally, whilst admitting that the first has almost equal justification.

Ethylic benzylimidophenylpropionate (or benzylamidocinnamate) melts at 68° . Benzylimidoacetophenone melts at 43 — 44° , and benzylimido-benzophenone, $CPh_2\cdot N\cdot CH_2Ph$, at 64° ; benzylimidoanisyl phenyl ketone forms an oil which possibly is a mixture of two isomerides.

Ethylic acetoacetate diphenylhydrazone is obtained first in the α -form; this melts at 120 — 135° , yielding a yellow liquid, the β -form, which does not solidify when cooled, although it is slowly reconverted into the α -form when kept at the ordinary temperature. Ethylic benzoylacetate diphenylhydrazone melts at 109 — 110° . C. F. B.

Preparation of Meta-, Chloro-, Bromo-, and Iodo-salicylic Acids. By TH. VAN WAVEREN (*Arch. Pharm.*, 1897, 235, 566—570).—Monhalogen substituted salicylic acids are readily obtained by the oxidation of chloro-, bromo-, or iodo-salicin with potassium permanganate, and subsequent hydrolysis with hydrochloric acid; they prove to be identical with the known meta-acids. Metachlorosalicylic acid forms white needles melting at 172° , the corresponding bromo-acid melts at

165°, and the iodo-acid at 196°. The *barium*, *sodium*, *potassium*, and *silver* salts of the latter acid are described.

Hydroxysalicylic acid, $C_6H_2(OH)_2 \cdot COOH$ [$COOH : (OH)_2 = 1 : 2 : 5$], obtained by fusing iodosalicylic acid with caustic potash, separates from hot water in colourless crystals melting at 199°. Its solution is coloured blue by ferric chloride, turning to red on the addition of sodium hydrogen carbonate. It is readily converted into quinol, thus proving the meta-position of the second hydroxyl group and of the iodine atom in the iodosalicylic acid from which it is formed. (Compare Visser, this vol. i, 202).
A. W. C.

Transformation of Unsaturated α -Hydroxy-acids into the Isomeric γ -Ketonic and α -Ketonic Acids.—By RUDOLPH FITTIG (*Annalen*, 1897, 299, 1—49. Compare Abstr., 1897, i, 14).—[With MAX GINSBERG.]—Experimental evidence is adduced in support of the statement (Abstr., 1895, i, 533) that the so-called phenylhydroxy-crotonic acid is identical with benzoylpropionic acid.

Benzoylbromopropionic acid, $COPh \cdot CHBr \cdot CH_2 \cdot COOH$, arises from the action of bromine on the unsaturated lactone produced by treating benzoylpropionic acid with acetic anhydride, the intermediate dibromocompound losing hydrogen bromide under the influence of atmospheric moisture. It crystallises in the triclinic system; $a : b : c = 0.64332 : 1 : 0.5399$. $\alpha = 74^\circ 42' 53''$. $\beta = 104^\circ 25' 52''$. $\gamma = 92^\circ 44' 15''$.

α -Hydroxy- γ -phenylcrotonic acid (Abstr., 1897, i, 14) crystallises from water in aggregates of needles, and melts at 137°. The *barium* and *calcium* salts are anhydrous; the *silver* salt dissolves with difficulty in cold water, and is decomposed when the liquid is boiled. The *amide* crystallises from boiling water in colourless leaflets, and melts at 141.5°.

[With NICOLAUS PETKOW.]— $\beta\gamma$ -Dibromo- α -hydroxy- γ -phenylbutyric acid, $CHPhBr \cdot CHBr \cdot CH(OH) \cdot COOH$, is obtained by the action of bromine on α -hydroxyphenylcrotonic acid dissolved in chloroform; it separates from the solvent in small, prismatic crystals, and becomes violet at 151°, melts to a reddish-violet liquid, and evolves gas at 155°. It dissolves in hot water, yielding bromodihydroxyphenylbutyrolactone (E. Fischer and Stewart, Abstr., 1892, 1447).

α -Hydroxyphenylcrotonic acid yields $\beta\gamma$ -phenylisocrotonic acid on reduction with sodium amalgam.

Benzylpyruvic (γ -phenyl- α -ketobutyric) acid, $CH_2Ph \cdot CH_2 \cdot CO \cdot COOH$, is produced when α -hydroxyphenylcrotonic acid is heated with 5 per cent. caustic soda during 2 hours; it dissolves with great readiness in ether, benzene, and chloroform, being sparingly soluble in carbon bisulphide, and almost insoluble in petroleum. It crystallises in lustrous plates, and melts at 46°; the aqueous solution deposits the acid in leaflets which also melt at 46° and contain $1\frac{1}{2}H_2O$. The *calcium* and *barium* salts crystallise in leaflets containing $1H_2O$, and the *silver* salt becomes brown when boiled with water. The *phenylhydrazone* crystallises from alcohol in prisms, and melts at 144—145°; the *amide* melts at 179—180°.

α -Hydroxy- γ -phenylbutyric acid, $CH_2Ph \cdot CH_2 \cdot CH(OH) \cdot COOH$, is obtained by reducing the foregoing acid in aqueous solution with 4

per cent. sodium amalgam, carbonic anhydride being passed through the liquid; it crystallises from a mixture of ether and petroleum in colourless leaflets, and melts at $104.5-105^{\circ}$. The *silver* salt is sensitive towards light, and is decomposed by boiling water.

[With MILTON FR. SCHAAK.]— α -Hydroxypentenoic acid (Abstr., 1897, i, 15) remains liquid at -18° . The *calcium* salt contains $3H_2O$, the *zinc* salt $2\frac{1}{2}H_2O$, whilst the *barium* salt is anhydrous; the *silver* salt crystallises from warm water in slender needles.

$\beta\gamma$ -Dibromo- α -hydroxyvaleric acid, $CHMeBr \cdot CHBr \cdot CH(OH) \cdot COOH$, obtained by the action of bromine on α -hydroxypentenoic acid dissolved in chloroform, crystallises in needles, and when freshly prepared melts indefinitely at $60-79^{\circ}$; after remaining for 10 days in the desiccator, it melts at $104-105^{\circ}$.

Details of experiments are recorded, showing that during the conversion of α -hydroxypentonic acid into levulinic acid under the influence of dilute hydrochloric acid (*loc. cit.*), the hydroxylactone, $C_5H_8O_3$, is formed as an intermediate product. M. O. F.

Remarkable Conversion of an α -Ketonic Acid into the Corresponding α -Amido-acid. By EMIL ERLÉNMEYER, jun. (*Ber.*, 1897, 30, 2976—2981).—The lactimide (m. p. 187°) obtained by the action of ammonia on α -benzamido-cinnamic acid (Abstr., 1893, i, 582) is shown to be identical with the compound obtained by the action of ammonia on phenylpyruvic acid. When ammonia reacts with α -benzamido-cinnamic acid, equivalent quantities of the lactimide and of benzamide are formed, thus proving that the lactimide cannot contain the benzoyl group. The acid, $C_{17}H_{17}NO_3$, which is formed when the lactimide is hydrolysed with hydrochloric acid or alkali, has the constitution $CH_2Ph \cdot CH(COOH) \cdot NH \cdot CO \cdot CH_2Ph$, since, when heated with concentrated hydrochloric acid, it yields phenylacetic acid and phenylalanine hydrochloride. Attempts are being made to synthesise the acid and thus prove its constitution. As the lactimide is readily obtained by the action of ammonia on the ethylic salt of the acid $C_{17}H_{17}NO_3$, it is regarded as the corresponding acid amide.

J. J. S.

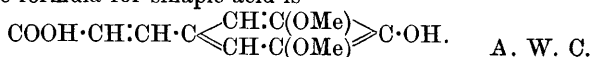
Synthesis of Tyrosine. By EMIL ERLÉNMEYER, jun., and JOHN T. HALSEY (*Ber.*, 1897, 30, 2981—2982).—Parahydroxybenzaldehyde, when warmed on the water bath with hippuric acid in the presence of acetic anhydride and fused sodium acetate, yields a yellow *lactimide* (compare Abstr., 1893, i, 580) which, when hydrolysed with sodium hydroxide, yields parahydroxy- α -benzamido-cinnamic acid; this, when reduced with sodium amalgam, gives benzoyltyrosine, and the latter, when heated in sealed tubes with fuming hydrochloric acid, yields tyrosine.

J. J. S.

Sinapic Acid. By JOHANNES GADAMER (*Arch. Pharm.*, 1897, 235, 570—577. Compare Abstr., 1897, i, 360).—When acetyl-sinapic acid is treated with potassium permanganate, there is formed a crystalline substance melting at 167° , which is acetylsyringic acid (m. p. $181-183^{\circ}$), for although the melting point differs considerably, on hydrolysis with baryta water syringic acid is obtained crystallising

from water in long, nacreous crystals melting at 202° . The identity of the two substances was further proved by the preparation of the methylic and barium salts. From this it follows that, in sinapic acid, the methoxyl and hydroxyl groups are in the same position as in syringic acid, that is, a symmetrical one, where the hydroxyl is in the para-position relatively to the side chain.

On oxidising sinapic acid with chromic mixture, dimethoxyquinone is produced in glistening, golden yellow prisms melting at 249° , thus definitely proving the para-position of the hydroxyl group to the side chain, and as the methoxyl and hydroxyl groups together are to the side chain as $[3:4:5]:1$, and, as already shown, the hydroxyl group is in position 4, then the methoxy-groups must occupy the positions 3 and 5, and the formula for sinapic acid is



β -Benzoylpropionic Acid. By MAX KUGEL (*Annalen*, 1897, **299**, 50—66. Compare this vol., i, 196).—The *phenylhydrazonohydrazide* of β -benzoylpropionic acid, $\text{CPh}(\text{N} \cdot \text{NHPH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPH}$, obtained by heating the acid with phenylhydrazine on the water bath, crystallises from alcohol in prisms, and melts at 195° . The solution in concentrated sulphuric acid becomes violet with ferric chloride.

The *anhydride*, $\text{CPh} \begin{array}{c} \swarrow \text{CH}_2 \cdot \text{CH}_2 \\ \searrow \text{N} - \text{NPh} \end{array} \text{CO}$, is produced along with it, and separated by means of its greater solubility in alcohol, from which it crystallises in slender needles melting at $98-99^{\circ}$.

The lactone obtained on heating benzoylpropionic acid with acetic anhydride undergoes oxidation when the alcoholic solution is boiled with ferric chloride; the *compound*, $\text{C}_{20}\text{H}_{12}\text{O}_4$, separates from the liquid in lustrous, dark red crystals having a bluish reflex; after crystallisation from boiling xylene, it melts at 135° . *Diphenacylfumaric acid*, $\text{COPh} \cdot \text{CH}_2 \cdot \text{C}(\text{COOH}) : \text{C}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COPh}$, which is probably the compound obtained by the action of alcoholic potash on the foregoing oxidation product, crystallises from ether in yellowish prisms, and, without melting, passes into the compound, $\text{C}_{20}\text{H}_{12}\text{O}_4$, from which it is produced. The *silver* salt is insoluble in alcohol, ether, and water. The *compound*, $\text{C}_{20}\text{H}_{12}\text{O}_4$, isomeric with the red oxidation product already mentioned, is obtained by heating diphenacylfumaric acid with glacial acetic acid; it crystallises in slender, yellow prisms, and sublimes without fusion when heated. It is insoluble in ether and light petroleum, and sparingly soluble in boiling alcohol and glacial acetic acid; chloroform, boiling xylene, and boiling benzene dissolve it, however, forming solutions which exhibit a beautiful greenish fluorescence. The solution in concentrated sulphuric acid is brownish-red.

The *compound*, $\text{C}_{20}\text{H}_{14}\text{O}_3$, obtained by heating β -benzoylpropionic acid with benzoic chloride for 12 hours on the water bath, crystallises from dilute alcohol in slender prisms, and melts at $191-192^{\circ}$.

Methylic benzoylpropionate melts at $18-20.5^{\circ}$, and boils at $187-187.5^{\circ}$ under a pressure of 30 mm. The *ethylic* salt melts at $18-19.5^{\circ}$, and boils at 192.5° under a pressure of 33 mm.; when heated with alcoholic ammonia at 100° during 5—6 hours, it does not yield the amide, but

gives rise to two other nitrogenous compounds. The *compound*, $C_{10}H_9NO$, crystallises from alcohol in lustrous, orange prisms; it gradually becomes red when heated, darkens at $220-225^\circ$, and melts at 233° . The *compound*, $C_{10}H_7NO$, crystallises in yellowish-green leaflets with bronze reflex, appearing bluish under the microscope; it crystallises from aniline, and sublimes when strongly heated. A third substance of uncertain composition is separated from the red mother liquor on dilution with water. M. O. F.

Action of Hübl's Reagent on Tannic Acids and on Tannin Extracts. By CARL BOETTINGER (*Chem. Zeit.*, 1897, 21, 460—461).—In previous communications (this vol., i, 30, 87), it has been shown that the acetyl derivatives of gallic and tannic acids give no "iodine number," whereas the free acids react with Hübl's reagent, but the "iodine number" varies with the amount and concentration of the iodine solution. Further experiments with tannic acids of different origin, oak bark, oak wood, and pine wood, and of their acetyl derivatives, confirm the former experiments. The action of Hübl's reagent on the following extracts has also been studied: Sumach, 165; algarobilla, 114; oak bark, 106; pine bark, 99; oak wood, 29; valonia, 153; quebracho, 188; terra japonica, 202; catechu pegu, 164; canaigre, 119. The numbers give the mean "iodine numbers." J. J. S.

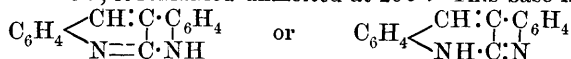
Optical Behaviour of Tannin. By PAUL WALDEN (*Ber.*, 1897, 30, 3151—3156. Compare Schiff, *Abstr.*, 1896, i, 370).—The optical activity of commercial tannin has led H. Schiff to discuss a formula by which the substance is represented as containing an asymmetric carbon atom. The author's experiments, however, show that the tannin at present obtainable is not only a mixture, but also varies in composition; application of its optical behaviour to the question of its structure is, therefore, inadmissible.

It is suggested that the comparatively high optical activity of commercial tannin may be due to the exaggeration of the rotatory power of a small proportion of active impurity by the tannin itself.

M. O. F.

Orthodinitrocyano-dibenzyl. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, 30, 3017—3022).—This substance (Bamberger, *Abstr.*, 1887, 131) is best obtained by dissolving powdered potassium cyanide (10.7 grams) in boiling methylic alcohol (260 c.c.), adding ortho-nitrobenzyl chloride (26 grams) and boiling for $\frac{3}{4}$ hour; the alcohol is then distilled off, the residue heated with water, and the oil, which solidifies after a while, recrystallised from a mixture of acetic acid (20 c.c.) and alcohol (5 c.c.); the substance is then pure enough for further use. When it is boiled for $1\frac{1}{2}$ hours with a mixture of equal volumes of hydrobromic acid (sp. gr. = 1.47) and acetic acid, it is hydrolysed to *orthodinitro-dibenzyl- α -carboxylic acid*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(COOH) \cdot C_6H_4 \cdot NO_2$, which melts at 170° . When this is reduced with ferrous hydroxide, or when orthodinitrocyano-dibenzyl is heated with alcoholic ammonia at 100° , a yellow monacid base, $C_{15}H_{10}N_2$, melting at $342-343^\circ$, is obtained; the yellow *hydrochloride* melts at about 280° , and the yellowish-white *monacetyl* derivative at 185° ; a yellow *mononitro*-derivative

was also obtained ; it remained unmelted at 290°. This base is possibly



and its formation has some analogy with the condensations observed by the author (Abstr., 1894, i, 603), and Reissert (Abstr., 1893, i, 687; 1894, i, 626). C. F. B.

Oxidation of Paranitrotoluenesulphonic Acid. By ARTHUR G. GREEN and ANDRÉ R. WAHL (*Ber.*, 1897, 30, 3097—3101. Compare Ris and Simon, this vol., i, 143).—4 : 4'-dinitrodibenzyl-2 : 2'-disulphonic acid, $\text{C}_6\text{H}_4[\text{C}_6\text{H}_3(\text{NO}_2)_2\text{SO}_3\text{H}]_2$, is most readily obtained by the oxidation of sodium nitrotoluenesulphonate with sodium hypochlorite. The sodium salt (100 grams) is dissolved in water (1 litre) and added to a 30 per cent. caustic soda solution (500 c.c.), the hypochlorite solution (220 c.c. of solution containing 7 per cent. of active chlorine) is slowly run in, while the temperature is kept at 40—50° and the mixture rapidly stirred. In this reaction, it is necessary to add the hypochlorite gradually, so that no colour is developed. The mixture is still kept well stirred after the addition of the hypochlorite, and is tested from time to time with potassium iodide starch paper ; when the iodide reaction becomes faint, the mixture is cooled and poured into 2 litres of cold water. The sparingly soluble sodium salt is then collected, washed with sodium chloride solution, and freed from a small quantity of dinitrostilbenedisulphonic acid by dissolving it in water and adding cold potassium permanganate solution. The free acid crystallises in colourless plates ; when dissolved in cold caustic soda solution and then treated with a reducing agent, it does not yield a red coloration, whilst the corresponding stilbene derivative does give a colour ; from this the authors conclude that Ris and Simon's acid must have contained a small quantity of the latter. It is also stated that this acid is identical with Bender's acid (Abstr., 1895, i, 287).

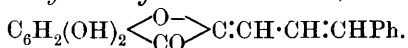
4 : 4'-dinitrostilbene-2 : 2'-disulphonic acid is obtained by a somewhat similar process. The sodium nitrotoluenesulphonate is dissolved in 2 litres of water, sodium hydroxide added, and then 500 c.c. of the sodium hypochlorite run in, the temperature being kept at 50° until all trace of hypochlorite has disappeared ; on cooling, the sodium salt of the sulphonic acid crystallises out. The *free acid* crystallises in colourless needles, and is readily soluble in water. The *alkali* salts are readily soluble in hot water, moderately in cold, but almost insoluble in saline or alkaline solutions. The *aniline* and *phenylhydrazine* salts of both acids are colourless and very sparingly soluble. When sodium dinitrostilbenedisulphonate is oxidised with cold potassium permanganate, the chief product is sodium paranitrobenzaldehydorthosulphonate. J. J. S.

A Colouring Matter from Anhydrobisdiketohydrindene. By CARL T. LIEBERMANN (*Ber.*, 1897, 30, 3137—3144).—Anhydrobisdiketohydrindene, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} : \text{C} \end{array} \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{C} : \text{C} \end{array} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{C} : \text{OH}$, readily yields blue colouring matters with bases, condensation taking place between molecular proportions of the two constituents, with elimination of the elements of water. These compounds closely resemble the correspond-

ing colouring matters obtained from cœrulignone, which, however, are formed from 2 mols. of the base. Colouring matters have been thus obtained from aniline, toluidine, ψ -cumidine, parachlor- and parabrom-aniline, metamidobenzoic acid, α - and β -naphthylamine, metamidophenol, amidothymol, paranisidine, sodium sulphanilate orthotolylene-diamine, paraphenylenediamine, paradiamidodiphenylmethane, and others, whilst no reaction is given by secondary or tertiary amido-compounds. The same substances may be obtained, but in much smaller yield, from diketohydrindene itself, which is probably first converted into the anhydro-compound. They are decomposed into their constituents when heated with hydrochloric acid, and are insoluble in dilute alkalis, but soluble in aqueous alkalis on boiling; and readily in alcoholic solutions of the alkalis.

Anhydrosdiketohydrindeneparatoluidide, $C_{18}H_{10}O_2 \cdot N \cdot C_6H_4Me$, crystallises in needles which have a dark metallic lustre and form an orange-red solution in concentrated sulphuric acid. The other compounds are very like this in all their properties. No analogous compounds have been obtained from any other of the derivatives of diketohydrindene. With paratoluidine, phenyldiketohydrindene yields a *toluidide*, $C_6H_4 \left\langle \begin{array}{c} \text{CO} \\ \text{C}(N \cdot C_7H_7) \end{array} \right\rangle CHPh$, which melts at 244° . A. H.

3:4-Dihydroxycinnamylidenecumaranone. By R. HALLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1897, 30, 2947—2952).—Compounds containing the chromophore, $CO \cdot C : C \cdot C : C$, have, as a rule, a redder shade than those containing the simpler group $CO \cdot C : C$. A substance of the former class, which is capable of dyeing mordanted cloth, is 3:4-*dihydroxycinnamylidenecumaranone*,



this, which is obtained when cinnamaldehyde is treated with 3:4-dihydroxycumaranone in presence of dilute aqueous soda, crystallises in brownish-yellow plates or needles and yields a magenta-red coloured solution in sulphuric acid. With alumina mordants, it produces a slightly redder shade than the corresponding benzylidene derivative; it moreover gives a violet solution with alkalis, whereas the benzylidene-compound yields a red solution. *Diacetylcinnamylidenecumaranone*, crystallises in long, yellow needles melting at 176° , and decomposes on exposure to light. *Diethoxycinnamylidenecumaranone* crystallises in tufts of yellow needles melting at 123° . A. H.

Oxidation of Naphthalene with Permanganate. By JOHN PROCHÁZKA (*Ber.*, 1897, 30, 3108—3109. Compare Henriques, *Abstr.*, 1888, 842).—Naphthalene suspended in hot water and well agitated by the aid of an automatic stirrer, is readily oxidised at 100° by permanganate solution to phthalonic acid; this, in its turn, can be oxidised by manganese peroxide and acid to phthalic acid. Seventeen grams of phthalic acid were obtained with 100 grams of commercial permanganate. The unoxidised naphthalene can readily be recovered. J. J. S.

Ethereal Oil of Angostura Bark. By HEINRICH BECKURTS and JULIUS TROEGER (*Arch. Pharm.*, 1897, 235, 634—640. Compare this vol., i, 37).—The authors have previously shown that when this crude left-handed oil is treated with acetic anhydride, it yields a right-handed terpene (18° in 100 mm. tube), which they called galipene. If phosphoric anhydride is used instead of acetic anhydride, inversion does not take place, and the terpene formed is of a clear green colour, and has the same boiling point as galipene, but is levorotatory (rotation = -10° in 100 mm. tube).

The fraction of crude oil boiling between 260° and 270° , when treated with phosphoric anhydride, gives an inactive sesquiterpene of a bluish-green colour, boiling at 256 — 260° .

When the right-handed terpene (galipene) is treated with a mixture of water, glacial acetic acid, and sulphuric acid, the elements of water are not directly added on to the terpene, but inversion takes place, and an inactive terpene is formed: whereas the raw angostura oil, under similar conditions, yields a second right-handed terpene (rotation = $+8.5^\circ$ in 100 mm. tube). Neither this terpene nor the left-handed and the inactive varieties give additive products when treated with glacial acetic acid and hydrogen chloride or bromide, thus differing from the so-called galipene. The authors are unable to account for this difference in behaviour, but are continuing the investigation with larger amounts of material.

A. W. C.

Ethereal Oils. By EDUARD GILDEMEISTER and KARL STEPHAN (*Arch. Pharm.*, 1897, 235, 582—592).—*Mandarin oil*, from *Citrus madurensis*, Loureiro, has a sp. gr. = 0.855 at 15° , and rotatory power $\alpha_D = +69^\circ 54'$ at 16° . It distils almost completely between 175° and 179° , and consists for the most part of right-handed limonene. The residue from the distillation, of which large amounts are now being worked up, appears to contain citral and citronellal.

Culilawan oil, from *Cinnamomum Culilawan*, has a sp. gr. = 1.051, and is soluble to a clear solution in three parts of alcohol; it contains from 61—62 per cent. of eugenol, together with small amounts of methyleugenol, and a substance boiling at 100 — 125° (10 mm.), the constitution of which has not been definitely decided.

Rosemary oil contains pinene (right and left-handed) as a normal constituent, and also inactive camphene.

Oil from the berries of Schinus molle, L. has a sp. gr. = 0.8505, rotatory power $\alpha_D = +46^\circ 4'$ at 17° , and, with sodium nitrite and acetic acid, gives an intense phellandrene reaction. It consists of about half a per cent. of pinene, phellandrene (right mixed with a little left-handed) and carvacrol, not thymol, as Spica (*Gazzetta*, 1884, 14, 204) has stated.

A. W. C.

Salicin and its Derivatives. By ERNST A. SCHMIDT (*Arch. Pharm.*, 1897, 235, 536—544).—This is a summary of the results obtained by Visser and van Waveren (following abstracts and this vol., i, 196).

E. W. W.

Halogen-substituted Compounds of Salicin and its Derivatives. By H. L. VISSER (*Arch. Pharm.*, 1897, 235, 544—560).—See preceding abstract. Iodine does not act on salicin directly, but the

moniodo-derivative is obtained when chloride of iodine acts on an aqueous solution of salicin. Chlorosalicin melts at 154° , bromosalicin at 170° , and iodosalicin at 192° . These derivatives all crystallise in fine, white needles containing $2\text{H}_2\text{O}$, form red solutions in concentrated sulphuric acid, but give no reaction with ferric chloride. By the action of acetic anhydride, tetracetyl derivatives are formed; *tetracetyl-chlorosalicin* melts at 142° , *tetracetyl-bromosalicin* at 148° , and *tetracetyl-iodosalicin* at 119° . With emulsin, these compounds yield monhalogen derivatives of saligenin, and they give a blue coloration with ferric chloride. Chlorosaligenin melts at 93° , bromosaligenin at 113° , and iodosaligenin at 138° ; attempts to obtain these compounds by the direct action of the halogen on saligenin failed, except in the case of the iodine derivative. When bromine acts on saligenin in alcoholic solution, tribromophenol is produced, and when bromine is added to an aqueous solution of saligenin made alkaline by sodium hydroxide, tribromosaligenin is formed as well as tribromophenol, whilst iodine added to an aqueous alkaline solution of saligenin gives iodosaligenin or di-iodosaligenin, according to the conditions. The monhalogen derivatives of saligenin, on oxidation with chromic mixture, yield the corresponding derivatives of salicylaldehyde and salicylic acid, and these are easily separated by distillation with steam. *Chlorosalicylaldehyde* melts at 99° , *bromosalicylaldehyde* at 104° , and *iodosalicylaldehyde* at 102° ; chlorosalicylic acid at 167° , bromosalicylic acid at 164° , and iodosalicylic acid at 196° ; these substituted aldehydes and acids give bluish violet colorations with ferric chloride in alcoholic solution.

[With TH. VAN WAVEREN.]—With hydroxylamine, the aldehydes form the corresponding aldoximes of which the chlorine compound melts at 122° , the bromine at 129° , and the iodine at 135° ; by boiling with acetic anhydride, the aldoximes yield monacetyl-substituted derivatives of the corresponding nitrile. Chlorosalicylic acid is a meta-compound [$\text{COOH} : \text{OH} : \text{Cl} = 1 : 2 : 5$], for its melting point and the properties of its barium and silver salts are identical with those of the acid prepared by Hasse (Abstr., 1878, 416) and Varnholt (*J. pr. Chem.*, **36**, 16) from parachlorophenol. The chlorine in monochlorosalicylaldehyde is also in the meta-position, for this substance can be converted into the same monochlorosalicylic acid by means of its oxime. Similarly, chlorosalicin is a meta-compound, as the glucoside of chlorosalicylic acid prepared from it is decomposed into glucose and metachlorosalicylic acid. The identity of bromosalicylic acid with the meta-acid obtained by Hübner and Brencken (this Journal, 1873, 756) by direct bromination of salicylic acid indicates also the meta-composition of the bromine derivatives. E. W. W.

Helicin. By TH. VAN WAVEREN (*Arch. Pharm.*, 1897, **235**, 561—566).—By the oxidation of chloro-, bromo- or iodosalicin with nitric acid, it was hoped that the corresponding halogenated helicens would be obtained, instead of which dihalogen substitution products of helicoidin, $\text{C}_{26}\text{H}_{32}\text{X}_2\text{O}_{14}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are produced.

Bromohelicin, $\text{C}_{13}\text{H}_{15}\text{BrO}_7$, may be obtained, by modifying the action of nitric acid on bromosalicin, as white needles melting at 160° . Sulphuric acid hydrolyses it, with production of glucose and metabromo-

salicylaldehyde. This same substance mixed with bromohelicoidin or a polymerisation product is formed by the direct action of bromine on helicin.

Chlorohelicin, prepared by the action of chlorine on helicin, forms white needles melting at 166° , easily soluble in hot alcohol and water, and yielding glucose and metachlorosalicylaldehyde on hydrolysis, for which reason the author proposes the following formula for chloro- or bromo-helicin, where $X = \text{Cl, Br}$,

$$\begin{array}{c} \text{CX} \cdot \text{CH} : \text{C} \cdot \text{COH} \\ | \\ \text{CH} \cdot \text{CH} : \text{C} \cdot \text{O} \cdot \text{C}_6\text{H}_{11}\text{O}_5 \end{array}$$

Iodohelicin could not be obtained by the action of nitric acid on iodosalicin, or of iodine chloride on helicin. A. W. C.

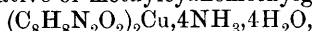
The Glucoside of *Saponaria Rubra*. By W. VON SCHULZ (*Chem. Centr.*, 1897, i, 302 and 446; from *Pharm. Zeit. Russ.*, **35**, 817—821, 833—839, 849—853).—Saporubrin, the active principle of *Saponaria rubra*, was first isolated by Kobert and Pachtorukow; details of the method employed are given. It must be distinguished from the sapotoxin of quillaja-bark, which it closely resembles. It is an amorphous powder, with a neutral reaction, and a taste which is at first cool, but becomes burning. Its aqueous solution gives a lather, and evolves carbonic anhydride; it is sparingly soluble in alcohol, but insoluble in the ordinary organic solvents. Concentrated sulphuric acid produces a reddish-brown coloration, which changes in the air, or on the addition of a drop of water, to a reddish-violet; this becomes emerald-green on adding potassium dichromate. Ferric chloride and alcoholic sulphuric acid produce a greenish-blue coloration. Barium hydroxide gives a white precipitate insoluble in water. Saporubrin rapidly reduces solutions of potassium permanganate and silver nitrate. It is optically active; $[\alpha]_D = -5.44$. Its constitution is expressed by the formula $(\text{C}_{18}\text{H}_{28}\text{O}_{10})_4$. The *benzoyl* derivative, $(\text{C}_{18}\text{H}_{25}\text{O}_{10}\text{Bz})_4$, melts at $208-210^{\circ}$.

The hydrolysis of saporubrin, with dilute sulphuric acid, gave varying amounts of sapogenin and glucose, according to the temperature; *sapogenins* having the formulæ $\text{C}_{17}\text{H}_{25}\text{O}_6$, $\text{C}_{18}\text{H}_{27}\text{O}_6$, $\text{C}_{18}\text{H}_{27}\text{O}_4$, $\text{C}_{14}\text{H}_{22}\text{O}_2$, were obtained, molecular weight determinations showing that these formulæ represent the molecular constitution of the substances. The *sapogenin* $\text{C}_{14}\text{H}_{22}\text{O}_2$ crystallises in microscopic needles, and melts at $248-250^{\circ}$; it is insoluble in water, easily soluble in alcohol, and soluble in ether, chloroform, methylic alcohol and glacial acetic acid. When freshly prepared, it dissolves in dilute alkalis. The *sugar* separated by the hydrolysis of saporubrin is not fermentable by yeast, and has $[\alpha]_D = +23.67$; its *glucosazone* melts at $165-170^{\circ}$.

The root of *Saponaria rubra* contains 3.45 per cent. of saporubrin. From its empirical formula, saporubrin appears to be a methylsapotoxin, and closely resembles the sapotoxins of *Agrostemma*, quillaja, *Sapindus* and *Saponaria alba*. An injection into the veins of dogs and cats of 2 milligrams of saporubrin per kilogram of body weight causes death. Taken inwardly, it causes vomiting; on being injected, it produces rapid nervous and muscular paralysis. It shows the property characteristic of the saponins of dissolving the red blood-corpuscles.

W. A. D.

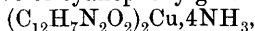
Some New Cuprammonium Compounds. By ICILIO GUARESCHI (*Chem. Centr.*, 1897, i, 368; from *Estr. d. Accad. Tor.*, 32). The author describes the preparation of a series of crystalline compounds of ammonia with the copper salts of the cyanhydropyridine derivatives dealt with in a former paper (Abstr., 1897, i, 168). Bluish-violet crystals of the *cuprammonium* derivative of cyanomethylglutaconimide, $(C_7H_5N_2O_2)_2Cu, 4NH_3, 2H_2O$, are obtained on adding copper sulphate to a solution of ammonium cyanomethylglutaconimide in aqueous ammonia; its composition is not altered by exposing it, in a vacuum, over calcium chloride. It is insoluble in cold water, but is decomposed by boiling water into ammonia, cupric oxide, and ammonium cyanomethylglutaconimide. At $100-125^\circ$, it loses water and is converted into a green compound, $(C_7H_5N_2O_2)_2Cu, 2NH_3$. The *cuprammonium* derivative of methylecyanomethylglutaconimide,



crystallises from ammonia, and on being dried in a desiccator loses all its contained water. From ethylcyanomethylglutaconimide a derivative, $(C_9H_9N_2O_2)_2Cu, 4NH_3$, is obtained which is insoluble in water; on being heated, it loses $3NH_3$ at 180° , whilst the fourth molecule is only given up when the salt decomposes.

Benzylacetoacetamide, $CH_2Ph \cdot CHAc \cdot CO \cdot NH_2$, obtained by treating ethylic benzylacetoacetate with ammonia, melts at $149-150^\circ$, and is converted by ammonia and ethylic cyanacetate into *benzylcyanomethyl-*

glutaconimide, $\begin{array}{c} CMe=C(CN) \cdot CO \\ | \\ CH(C_7H_7) \cdot C(OH):N \end{array}$; this yields a *cuprammonium* derivative, $(C_{14}H_{11}N_2O_2)_2Cu, 4NH_3, 2H_2O$, which crystallises in blue needles, and is converted at 110° into $(C_{14}H_{11}N_2O_2)_2Cu, 2NH_3$. The *cuprammonium* derivative of cyanophenylglutaconimide,



is a blue, crystalline powder; it loses $2NH_3$ at 180° , and is nearly insoluble in ammonia and in water.

The author points out that those of the salts which are anhydrous are the most stable. All the substances described contain $4NH_3$; to explain this, the presence of the group $(NH_3)_2 \cdot Cu : (NH_3)_2$ is assumed.

W. A. D.

Bromination of 1-Ethoxyquinoline. By ADOLPH CLAUS and HANS HOWITZ (*J. pr. Chem.*, 1897, [ii], 56, 390-392).—When 1-ethoxyquinoline (1 mol.) is treated with bromine (1 mol.) in acetic acid solution at the ordinary temperature, the dibromo-derivative is not formed. When the product is poured into water, 3:4-dibromo-1-hydroxyquinoline, melting at 196° , separates; whilst from the mother liquor, sodium acetate precipitates 4-bromo-1-ethoxyquinoline, and unchanged 1-ethoxyquinoline remains in solution. The bromethoxyquinoline melts at 55° ; it forms a yellowish-red *platinochloride*, with H_2O , which melts and decomposes at $218-220^\circ$, and is hydrolysed by hydrochloric acid at 180° yielding 4-bromo-1-hydroxyquinoline melting at 124° .

1-Ethoxyquinoline, when treated with hydrogen bromide in ethereal solution, yields a hygroscopic *hydrobromide*, which melts and decomposes at $222-223^\circ$; when this (1 mol.) is heated with bromine (1 mol.)

in chloroform solution, it yields a *dibromide* additive product. Boiling with water converts this into 4-bromo-1-ethoxyquinoline and resinous substances; heating at 200° converts it into 1-hydroxyquinoline and the 4-bromo- and 3:4-dibromo-derivatives of this. C. F. B.

Action of Sulphur Chloride on Aromatic Amines. By ALBERT EDINGER (*J. pr. Chem.*, 1897, [ii], 56, 273—282).—When 1-methylquinoline is mixed gradually with three times its weight of sulphur chloride, S_2Cl_2 , the mixture being cooled with ice at first, but afterwards heated for several hours at 160—170°, a crystalline substance may be obtained from the product by extracting this with dilute hydrochloric acid and cautiously neutralising the extract with ammonia. This substance melts above 360°, and its molecular formula is $(C_9NH_5S)_2$; it is thus isomeric with the substance obtained in a similar manner from quinoline (Abstr., 1897, i, 103), and the methyl group must therefore have become replaced by hydrogen. The yield of this new substance is small; it is oxidised by dilute nitric acid to nicotinic acid; it is not reduced by zinc dust and acetic acid; when it is sublimed under diminished pressure, only traces of hydrogen sulphide are formed, and no sulphur is removed when the vapour of the substance is passed over heated copper turnings; it has feebly basic properties.

When the chloride SCl_2 is employed instead of S_2Cl_2 , some of the same sulphur compound is obtained, together with 1:3-dichloroquinoline and a *tetrachloroquinoline* melting at 121°; and in one experiment a small quantity of a monochloroquinoline melting between 30° and 40° was isolated. The methyl has been largely replaced by chlorine in this case.

Neither 3-hydroxyquinoline, 1-hydroxyquinoline, isoquinoline nor pyridine yields a sulphur compound when treated with sulphur chloride; from the first three substances respectively there were obtained instead a mono-, a di-, and a tri-chloro-derivative, melting at 187°, 179°, and 124°. C. F. B.

Quinaldine-3'-carboxylic Acid. By ADOLPH CLAUS and ERNST MOMBERGER (*J. pr. Chem.*, 1897, 56, 373—389).—Ethylic 2'-methylquinoline-3'-carboxylate (quinaldine-3'-carboxylate), when nitrated at the ordinary temperature with a mixture of equal parts of nitric and sulphuric acids, yields a 1- and a 4-nitro-derivative, to the extent respectively of 45 and 40 per cent. of the theoretically possible amount; when the product is poured into water, the 4-nitro-compound remains in solution as the sulphate, whilst the 1-isomeride, being a weaker base, is precipitated. Neither ethylic salt forms a methiodide. Both are hydrolysed to the corresponding nitro-acids by heating with strong hydrochloric acid in an open vessel on the water bath, and from these acids, by heating them with 10 per cent. sulphuric acid at 150°, carbonic anhydride can be eliminated; the products are respectively yellow 1-nitro-2'-methylquinoline, which melts at 137° and is not volatile with steam, and colourless 4-nitro-2'-methylquinoline, which melts at 82° and does come over with steam (Buhl, *Diss. Freiburg i. B.*, 1897). Both ethylic salts, moreover, can be reduced by iron paste, with a drop of acetic acid, to the corresponding amido-compounds, and

these are hydrolysed by hydrochloric acid to the amido-acids, which can also be prepared by the reduction of the nitro-acids.

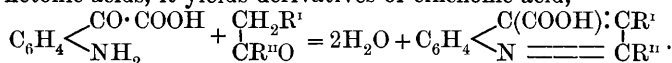
1-Nitro-2'-methylquinoline-3'-carboxylic acid is yellowish and melts and decomposes at 196°; the yellow *hydrochloride* decomposes at 204°; the *ethylic* salt is yellowish, melts at 137°, and forms an orange-yellow *platinochloride* (with 2H₂O) which decomposes at 195°. 1-Amido-2'-methylquinoline-3-carboxylic acid is straw yellow, and melts and decomposes at 230°; its *silver* salt was prepared and analysed; the *ethylic* salt is almost colourless, melts at 99°, forms an orange *platinochloride*, with 2H₂O, decomposing at 190°, and an orange *methiodide* decomposing at 170°, and can be converted by the Sandmeyer reaction into *ethylic* 1-chloro-2'-methylquinoline-3'-carboxylate, which melts at 92°, forms a yellow *platinochloride*, with 4H₂O, decomposing at 205°, but no *methiodide*, and is hydrolysed by strong hydrochloric acid to 1-chloro-2'-methylquinoline-3'-carboxylic acid, which is yellow and melts at 216°.

4-Nitro-2'-methylquinoline-3'-carboxylic acid is yellow and melts at 236°; the yellowish-red hydrochloride melts and decomposes at 215°; the ethylic salt is yellowish, melts at 126°, and forms a reddish-yellow platinumchloride, with 2H₂O, which decomposes at 232°. 4-Amido-2'-methylquinoline-3'-carboxylic acid is orange-yellow, and melts and decomposes at 275°; the ethylic salt is almost colourless, melts at 110°, and forms a reddish-orange platinumchloride, with 2H₂O, decomposing at 224° and a red methiodide which melts and decomposes at 198—200°.

2-Methylquinoline-3'-carboxylamide (quinaldine-3'-carboxylamide) separates gradually when the corresponding ethylic salt is allowed to remain for weeks with a large excess of the strongest ammonia in a well-stoppered bottle at the ordinary temperature, or, better, at 40—50°. The greater part of the ethylic salt, however, is converted into the ammonium salt.

C. F. B.

Condensation of Isatic Acid to form Derivatives of Cinchonic Acid. By WILH. PFITZINGER (*J. pr. Chem.*, 1897, [ii], 56, 283—320. Compare Abstr., 1886, 370; 1889, 412).—Isatic acid undergoes a series of reactions similar to those discovered by Friedländer in the case of orthamidobenzaldehyde (Abstr., 1892, 1106). With ketones and ketonic acids, it yields derivatives of cinchonic acid.



With acetaldehyde, it would not condense; it does react, however, with acetone, methyl ethyl ketone, acetophenone, deoxybenzoin, pyruvic acid, and ethylic acetoacetate. When the two radicles CH_2R^1 and R^n are of unequal size, it is the larger that reacts with the CO group of the isatic acid. The method commonly adopted was to heat the ketone with the isatic acid, dissolved in excess of aqueous-alcoholic potash of about 12 per cent. strength, for several hours on the water bath in a reflux apparatus; in the case of deoxybenzoin, which is easily acted on by alkalis, it was found advisable to add it gradually to the already boiling alkaline solution of isatic acid; pyruvic acid and ethylic acetoacetate reacted at the ordinary temperature with excess of 33 per cent. aqueous potash, no alcohol being used.

Acetone yields 2'-methylcinchonic acid, $C_9NH_5Me \cdot COOH$ (Böttiger, Abstr., 1884, 320); this has both acid and basic properties. The yellow *platinochloride* melts and decomposes at 220° , and crystallises with $2H_2O$; the hydrobromide crystallises from water with $2H_2O$, from moderately strong hydrobromic acid with H_2O ; the orange-red *dichromate* and the greenish-yellow *picrate*, the latter melting at $190-191^\circ$, are anhydrous; the *silver* salt was prepared and analysed, and many other salts are described. The *ethylic* salt, which was obtained by digesting the acid at the ordinary temperature with saturated absolute alcoholic hydrogen chloride, melts at 77° ; its yellow *picrate* melts at $155-156^\circ$, and its yellow *platinochloride* melts and decomposes at 203° and crystallises with $2H_2O$. By heating the ethylic salt for several hours with a large excess of aqueous ammonia of sp. gr. = 0.880, it is converted into the *amide*, which melts at 239° , and forms a *picrate* melting and decomposing at $231-232^\circ$. 2'-Methylcinchonic acid, when it is heated with phthalic anhydride and zinc chloride at $170-180^\circ$, forms a *phthalone*, $COOH \cdot C_9NH_5 \cdot CH : C < \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} > CO$, which melts and decomposes at some temperature above 300° .

Acetophenone yields 2'-phenylcinchonic acid, $C_9NH_5Ph \cdot COOH$ (Döbner, Abstr., 1887, 504); of this, the acid properties are well marked, but not so the basic, for the salts with acids are decomposed by water. The orange-yellow, anhydrous *platinochloride*, and the yellow *picrate* (not the normal compound, but $2C_9NH_5Ph \cdot COOH, C_6H_5N_3O_7$) were prepared and analysed; so also were the *calcium* and *silver* salts, with $2\frac{1}{2}$ and $\frac{1}{2}H_2O$ respectively, and the *ethylic* salt, which melts at $50-51^\circ$, and forms a greenish-yellow *picrate* melting at $144-145^\circ$, and a pale flesh-coloured *platinochloride* melting and decomposing at $210-211^\circ$. The acid itself is converted into 2'-methylquinoline by distillation with slaked lime.

Deoxybenzoin yields 2':3'-diphenylcinchonic acid, $C_9NH_4Ph_2 \cdot COOH$, which melts and decomposes at 295° , and has very feeble basic, but marked acid, properties. The yellowish-green *picrate* melts at 236° ; the *sodium* and *calcium* salts, with $8H_2O$ and $9H_2O$ respectively, and the *silver* salt were prepared and analysed, but no ethylic salt could be obtained. The acid, when heated a little above its melting point, yields a substance that melts at $90-91^\circ$ and boils at about 310° under 80 mm. pressure. This is probably 2':3'-diphenylquinoline (Buddeberg, Abstr., 1890, 1142); its greenish-yellow *picrate* melts at $223-224^\circ$, and it forms a yellow *methiodide*, which has the character of a quaternary iodide, and decomposes at 231° into methylic iodide and 2':3'-diphenylquinoline; the orange-red *platinochloride* of the corresponding *methochloride* was prepared and analysed.

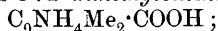
Pyruvic acid yields 2':4'-quinolinedicarboxylic acid, $C_9NH_5(COOH)_2$, (Döbner and Peters, Abstr., 1890, 176); this has no basic properties. The normal *potassium* salt, with $2\frac{1}{2}H_2O$, was prepared and analysed. When the acid is heated at 240° , it yields 4'-quinolinecarboxylic (cinchonic) acid, although, when it is distilled, quinoline is formed.

Methyl ethyl ketone yields 2:3-dimethylcinchonic acid,
 $C_9NH_4Me_2 \cdot COOH$,

which melts and decomposes above 310° ; when distilled with slaked lime, it yields 2':3'-dimethylquinoline (Rohde, Abstr., 1889, 523).

Ethylic acetoacetate yields 2'-methylquinoline-3':4'-dicarboxylic acid, $C_9NH_4Me(COOH)_2 + H_2O$, which melts and decomposes at $236-237^{\circ}$ when heated slowly; its *silver* salt was prepared and analysed.

Paramethylisatic acid reacts with acetone in the same manner as isatic acid; the product is 3:2'-dimethylcinchonic acid,



this melts and decomposes at 261° , and has both basic and acid properties; the flesh-coloured *platinochloride*, which melts and decomposes at $243-244^{\circ}$ and crystallises with $2H_2O$, and the *silver* salt were prepared and analysed. When the acid is distilled with lime, it yields 3:2'-dimethylquinoline (Döbner and Miller, Jacobsen and Reimer, Abstr., 1884, 184, 335).

C. F. B.

Existence of Condensation Rings with Para-Linking. II.

By ALBERT LADENBURG and W. HERZ (*Ber.*, 1897, 30, 3043—3045. Compare Abstr., 1897, i, 485).—Rosdalsky, by observing the depression of the freezing point of phenol brought about by the substance described by him as 1:4-methylenepiperazine, $C_4N_2H_8 \cdot CH_2$ (Abstr., 1896, i, 257), found the molecular weight of that substance to be 80—84 (calculated 98). The authors have obtained numbers varying irregularly between 52 and 79.5, from which they conclude that the substance is decomposed in phenol solution, and, as a matter of fact, it cannot be recovered from that solution. They regard it as a polymeride, in which case the assumption of a para-linking is no longer necessary.

C. F. B.

Tartrazines. By ROBERT GNEHM and LOUIS BENDA (*Annalen*, 1897, 299, 100—130. Compare Abstr., 1896, i, 678; also Anschütz, Abstr., 1897, i, 258).—In view of the constitutional formula for tartrazine put forward by Anschütz (*loc. cit.*), the authors have modified their formula for the colouring matter obtained by the action of paranitrodiazobenzene chloride on an alkaline solution of tartrazine, regarding it as having the constitution

$$\begin{array}{c} N \\ \parallel \\ N(C_6H_4 \cdot SO_3Na) \cdot CO \end{array} > C : N \cdot NH \cdot C_6H_4 \cdot NO_2.$$

The *barium* salt is an amorphous, orange-yellow powder, and dissolves in water with difficulty; the *silver* salt crystallises in cinnabar-red prisms, and forms a yellow solution in water.

The colouring matter itself is obtained also from paranitrophenylhydrazine, dihydroxytartaric acid, and paraphenyldiazinesulphonic acid; the yield, however, is small, owing to the fact that paranitrophenylhydrazine converts dihydroxytartaric acid into the osazone instead of the hydrazone.

Paranitrophenylhydrazinedihydroxytartaric *osazone* is prepared by the action of the hydrazine on dihydroxytartaric acid at common temperatures; it is a yellow substance which becomes red on exposure to air. It is somewhat soluble in hot water, forming a yellow solution, and it dissolves also in alcohol, becoming in part converted into the pyrazolone derivative; caustic alkalis give rise to a beautiful blue solution, which becomes dirty brown when diluted with much water.

Alcoholic ferric chloride develops a reddish-brown coloration which is taken up by ether. The osazone is capable of losing water in two ways, producing (1) a pyrazolone derivative, or lactazam, owing to elimination of water from one imido-group and the more remote carboxylic radicle and (2) an acid anhydride, by elimination of water from the two carboxylic groups. The first of these changes is brought about by heating the osazone with aqueous hydrochloric acid, glacial acetic acid, 95 per cent. alcohol, or a dilute solution of sodium carbonate; conversion into the anhydride, on the other hand, results from heating the osazone alone, or with acetic anhydride or benzoic chloride.

1-*Paranitrophenyl-3-carboxyl-4-paranitrophenylhydrazonepyrazolone* is the product of the former change; after crystallisation from acetic anhydride, it melts and decomposes at 238—240° (uncorr.). The solution in caustic soda is brown, and in concentrated sulphuric acid orange red. The *sodium* salt crystallises in orange needles or scales containing $1\text{H}_2\text{O}$, and the *barium* salt is anhydrous; the *silver* salt is brown, and the *mercurous* and *lead* salts orange.

The *anhydride*, $\text{C}_{16}\text{H}_{10}\text{N}_6\text{O}_7$, of the osazone, obtained by the second series of agents, crystallises from acetic anhydride in red prisms, and melts at 278—280°, when it becomes black and evolves gas. It is insoluble in boiling water, but slowly forms a reddish-brown solution in boiling sodium carbonate, which regenerates the osazone; the solution in caustic soda is blue, owing to the immediate production of the osazone.

The authors have repeated the experiments of Ziegler and Locher (Abstr., 1887, 578) who state that acetic anhydride converts diphenylizindihydroxytartaric acid into an acetyl-anhydride which melts at 234°; they find that this compound is not really an acetyl derivative, but an anhydride arising from the dehydrating action of acetic anhydride and of benzoic chloride. When this substance is boiled with a five per cent. solution of caustic soda, 1-phenyl-3-carboxyl-4-phenylhydrazonepyrazolone is produced.

Ziegler and Locher state that monophenylizindihydroxytartaric acid, the hydrazone of dihydroxytartaric acid, is produced from phenylhydrazine and the acid, even in presence of excess of the latter, when the action proceeds at common temperatures; this does not apply in the case of paranitrophenylhydrazine, which in the cold, and in the presence of excess of dihydroxytartaric acid, yields the osazone. The authors find that a mixture of osazone with hydrazone is produced in the case of phenylhydrazine, whilst metanitrophenylhydrazine yields principally osazone with a small proportion of hydrazone. M. O. F.

New Methods for the Preparation of Anhydro-compounds. By STEFAN VON NIEMENTOWSKI (*Ber.*, 1897, 30, 3062—3071).—It has been previously shown (Abstr., 1895, i, 571) that the amides of fatty acids readily react with orthamidobenzoic acid, yielding δ -hydroxyquinazoline derivatives. The condensation of acid amides and of ethereal salts with orthamidophenols and with orthodiamine hydrochlorides has now been investigated (compare Kelbe, Abstr., 1883, 915; R. Meyer and Seeliger, Abstr., 1896, i, 45). When equivalent quantities of formamide and of orthamidophenol are subjected to dry distillation, Ladenburg's benzoxazole melting at 30° is produced.

A theoretical yield of O. Fischer's 3-methylbenzimidazole is obtained by heating together formamide and metaparatolylenediamine hydrochloride [$\text{CH}_3 : (\text{NH}_2)_2 = 1 : 3 : 4$]; it melts at 114° . Acetamide and the same salt, when heated to 180° , give Hobrecker's ethenyltolylenediamine melting at $200-202^\circ$.

β -Phenylmetatolimidazole is obtained from benzamide and metaparatolylenediamine hydrochloride.

β -Orthamidophenylbenzimidazole, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, is formed when equivalent quantities of orthamidobenzamide and of orthophenylenediamine hydrochloride are heated at 190° for 3 hours; it is purified by rubbing in a mortar with strong alkali, and subsequent solution in hot alcohol, and can be freed from a dye which accompanies it by the addition of boiling water to the alcoholic solution and quick filtration, when the whole of the colouring matter will be found on the filter. The pure imidazole crystallises in colourless, flat, monoclinic prisms melting at 211° . It is readily soluble in boiling alcohol or chloroform, moderately in benzene or ether, and very sparingly in hot water. It dissolves readily in acids, but not in alkalis. Its *hydrochloride*, $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl}$, is only sparingly soluble in boiling alcohol or water and melts at 275° . The *platinochloride*, $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot \text{H}_2\text{PtCl}_6$, crystallises in yellow needles, blackens at $250-280^\circ$, and is readily decomposed in solution yielding metallic platinum.

β -orthamidophenylpara-(? meta)-tolimidazole is formed by the action of orthamidobenzamide on metaparatolylenediamine hydrochloride; it crystallises in pearly, glistening, six-sided plates melting at 189° . β -Orthamidoparatolylbenzimidazole, from orthophenylenediamine hydrochloride and orthamidotolylamide, crystallises from alcohol in glistening plates and from toluene in needles, melts at 203° , is readily soluble in cold acetone or acetic acid, in boiling alcohol or toluene, is but moderately soluble in ether, and practically insoluble in water. The *nitrate* is readily soluble, but the *hydrochloride*, $\text{C}_{14}\text{H}_{13}\text{N}_3 \cdot \text{HCl}$, and *sulphate* only sparingly. The product from orthamidotolylamide and metaparatolylenediamine hydrochloride crystallises in little rods melting at 188° . When orthamidophenol (20 grams) is boiled with ethyl acetate for 18 hours and the product subjected to fractional distillation, the chief products are orthacetamidophenol and β -methylbenzoxazole; metatolimidazole and ethylic chloride are the products formed when equivalent quantities of ethylic formate and metaparatolylenediamine are heated in sealed tubes for 3 hours at 225° . Similar experiments with ethylic acetate gave but a small quantity of ethenyldiamidotoluene.

J. J. S.

A Method of Preparing Phthalazines. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, 30, 3022—3037).—By acting with hydrazine on ketonic orthocarboxylic acids, $\text{CRO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, and treating the phthalazone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CR} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N}_2\text{H}$, which is formed with phosphorus oxychloride, a chlorophthalazine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CR} \\ \diagup \quad \diagdown \\ \text{CCl} \end{smallmatrix} \text{N}_2$, is obtained. When this is heated with hydriodic acid and phosphorus at

200°, a simple reduction to the phthalazine, $C_6H_4 \begin{smallmatrix} \text{CR} \\ \text{CH} \end{smallmatrix} N_2$, does not take place; one of the nitrogen atoms is eliminated as ammonia, and a dihydroisindole, $C_6H_4 \begin{smallmatrix} \text{CHR} \\ \text{CH}_2 \end{smallmatrix} NH$, is formed, occasionally also an isindole. It is now found that the desired reduction to a phthalazine can be effected, in the case of 4-chlorophthalazine and 1:4'-chloromethylphthalazine, by boiling these substances with hydriodic acid (boiling at 127°) and red phosphorus.

1':4'-Methylchlorophthalazine (Abstr., 1893, i, 348) is obtained by heating 1'-methylphthalazine (50 grams) for $\frac{1}{2}$ hour on the water bath with phosphorus oxychloride (100 c.c.) and pouring the product into ice and water. The orange-red *platinochloride*, $2C_9H_7ClN_2 \cdot H_2PtCl_6$, is still unmelted at 280°; the yellow *aurochloride*, $2C_9H_7ClN_2 \cdot HAuCl_4$, and *picrate*, $C_9H_7ClN_2 \cdot C_6H_3N_3O_7$, melt at 149–150° and 154° respectively; the red *ferrocyanide*, $2C_9H_7ClN_2 \cdot H_4Cfy$, crystallises in hexagonal plates. When methylchlorophthalazine is boiled for 1 hour with hydriodic acid and phosphorus, the product is 1':4'-methylidophthalazine, melting at 116°, the orange-yellow *platinochloride* of which, $2C_9H_7IN_2 \cdot H_2PtCl_6$, remains unmelted at 280°. When the boiling is continued for 9 hours or more, until there is no solid remaining in the flask except the phosphorus, 1'-methylphthalazine, $C_6H_4 \begin{smallmatrix} \text{CMe:N} \\ \text{CH=N} \end{smallmatrix}$, is

formed; this is deliquescent, melts at 74.5°, and boils at 204°, 210–213°, and 322–324° (with partial decomposition) under pressures of 25 mm., 40 mm., and 1 atm. respectively; some 1'-methylphthalazine and methylisindole are also formed in the reaction. 1'-Methylphthalazine behaves generally as a monacid base; the *hydrochloride* melts and decomposes at 222–223°, the yellowish *hydriodide* at 287°, and the lemon-yellow *aurochloride* and *picrate* at 175° and 205° respectively; the *nitrate* decomposes at 159°, the orange-red *dichromate* at 170°; the reddish-orange *ferrocyanide*, $2C_9H_7N_2 \cdot H_4Cfy$, is unmelted at 290°. Reduction with zinc and hydrochloric acid converts the base into methylisindole, not to a base $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CHMe \cdot NH_2$, as the analogy with phthalazine (Abstr., 1893, i, 732) would lead one to expect. Sodium amalgam does, however, reduce it to 1'-methyltetra-

hydrophthalazine, $C_6H_4 \begin{smallmatrix} \text{CHMe} \\ \text{CH}_2 \end{smallmatrix} N_2H_2$, a monacid base the *hydrochloride* and *picrate* of which melt and decompose at 190° and 146° respectively, whilst the *dibenzoyl* derivative melts at 185°. With methylic iodide in cold methyl-alcoholic solution, 1'-methylphthalazine forms a *methiodide* which melts and decomposes at 142–143°; when this is distilled with aqueous potash, the distillate contains 1':3'-*dimethylidihydrophthalazine*, $C_6H_4 \begin{smallmatrix} \text{CMe:N} \\ \text{CH}_2 \cdot NMe \end{smallmatrix}$, a monacid base the

hydrochloride of which melts at 245°, and the lemon-yellow *picrate* and orange-yellow *platinochloride* decompose at 120° and 230° respectively, whilst the residue in the flask contains 1':3'-*dimethylphthalazone*, $C_6H_4 \begin{smallmatrix} \text{CMe:N} \\ \text{CO} \cdot NMe \end{smallmatrix}$, which melts at 109–110°, and can also be prepared

by methylating 1'-methylphthalazone. 1'-Methylphthalazine exhibits some of the condensation reactions of 2'-methylquinoline (quinaldine): heated for three-quarters of an hour at 200—210° with phthalic anhydride in an atmosphere of carbonic anhydride, it yields a yellow phthalone, $\text{C}_6\text{H}_4-\text{C}(\text{CH}_3):\text{CH}:\text{C}_8\text{H}_4\text{O}_2$, melting at 260°; with excess of

chloral at 55—60°, it yields 1'-trichlorohydroxypropylphthalazine, $\text{C}_8\text{N}_2\text{H}_5\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$, which melts and decomposes at 180°, and is hydrolysed by methyl-alcoholic potash to phthalazine-1'-acrylic acid, $\text{C}_8\text{N}_2\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, which melts and decomposes at 200°, and is also a monacid base, the hydrochloride and yellow aurochloride decomposing at 218° and 166° respectively, whilst the picrate melts and decomposes at 157—158°, and the orange-red platinochloride is unmelted at 270°. With benzaldehyde at 100°, 1'-methylphthalazine yields the yellow 1'-cinnamenylphthalazine, $\text{C}_8\text{N}_2\text{H}_5\cdot\text{CH}:\text{CHPh}$, melting at 115°, which can be reduced by boiling with hydriodic acid and phosphorus to 1'-phenylethylphthalazine, $\text{C}_8\text{N}_2\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, melting at 112·5—113·5°, a monacid base of which the yellowish hydriodide melts at 212—220°, and the nitrate decomposes at 135—136°.

Incidentally, it is mentioned that the anhydride of diphtalaldehyde-hydrazonic acid (Liebermann and Bistrzycki, Abstr., 1893, i, 372) melting at 219—220°, is obtained when phthalazone is prepared from phthaldehydic acid by the action of hydrazine; and that, when 1'-methylphthalazone is methylated, the hydrazone-methiodide of acetophenonecarboxylic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}:\text{N}_2\text{H}_2\cdot\text{MeI}$, melting and decomposing at 201°, is formed. C. F. B.

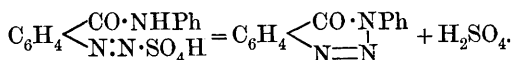
Syntheses in the Phenanthridine Group. By AMÉ PICTET and A. GONSET (*Chem. Centr.*, 1897, i, 413; from *Arch. Sci. phys. Genève*, [iv], 3, 37—51).—Orthophenylbenzaldehyde, $\text{C}_6\text{H}_4\cdot\text{Ph}\cdot\text{COH}$, formed when a mixture of calcium formate and calcium orthophenylbenzoate is distilled, is a bright yellow oil which boils at 310° without decomposition, and yields a phenylhydrazone melting at 115°; its oxime melts at 112·5°, and, on being heated with zinc chloride at 280—300°, loses H_2O , yielding phenanthridine.

When fluorenone oxime is heated with zinc chloride, the Beckmann transformation takes place, and a yield of 30 per cent. of phenanthridone is obtained.

Orthonitrobenzanilide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NPh}$, prepared from ortho-nitrobenzoic chloride and aniline, crystallises from alcohol or benzene in white needles, and melts at 155°. On reduction with ammonium sulphide, it yields orthamidobenzanilide, which crystallises from benzene in lustrous needles, and melts at 131°. On diazotising a sulphuric acid solution of this substance, and boiling, phenyl-β-phenotriazone,

$\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NPh}$
 $\text{C}_6\text{H}_4\cdot\text{N}=\text{N}$, is obtained, instead of phenanthridone; this crystallises from dilute alcohol in slender needles, melts at 150—151°, is almost insoluble in water, ether, and light petroleum, more soluble in alcohol and benzene, and very soluble in chloroform; its formation is explained by assuming a separation of sulphuric acid to take place

from the benzanilide-diazosulphate, according to the following equation.



In order to avoid such a separation, it is necessary to employ an anilide in which an alkyl radicle is substituted for the hydrogen of the imido-group. *Orthonitrobenzoylmethylanilide*, prepared from methylaniline and orthonitrobenzoic chloride, crystallises in white needles, and melts at 94.5°. *Orthamidobenzoylmethylanilide* crystallises from benzene in prisms and melts at 127°. When diazotised in hydrochloric acid solution, and heated, nitrogen is evolved, and *n*-methylphenanthridone (Pictet and Patri, Abstr., 1893, i, 722), is obtained.

When benzanilide is distilled through a red-hot tube packed with pumice, a molecule of hydrogen is eliminated and phenanthridone is formed; benzyaniline, when similarly treated, yields a mixture of phenanthridine and acridine, together with a primary base, which is probably paramidodiphenylmethane, formed by the molecular transformation of benzyaniline. The formation of acridine is explained by assuming that ortho- as well as paramidodiphenylmethane results from this transformation, and that this, by the loss of 2H₂, is transformed into acridine (compare Abstr., 1894, i, 200).

W. A. D.

Action of Chloroform and Alcoholic Potash on Phenylhydrazine. By SIEGFRIED RUHEMANN (*Ber.*, 1897, 30, 2869—2871. Compare Ruhemann and Elliott, *Trans.*, 1888, 53, 850).—The compound produced by the action of chloroform and alcoholic potash on phenylhydrazine (*loc. cit.*) is also obtained by heating formophenylhydrazide (Abstr., 1897, i, 468), and has been called diphenyltetrazoline by Pellizzari (Abstr., 1897, i, 231).

Amidodiphenyltetrazoline, C₁₄H₁₁N₄·NH₂, obtained by reducing nitrodiphenyltetrazoline with stannous chloride and hydrochloric acid, crystallises from dilute alcohol in needles, and melts at 188°. The *hydrochloride* forms colourless needles.

M. O. F.

The Alleged Synthesis of Xanthine from Hydrogen Cyanide. By EMIL FISCHER (*Ber.*, 1897, 30, 3131—3133).—The author has repeated Gautier's experiments (Abstr., 1885, 275), who, by heating hydrogen cyanide with acetic acid at 145°, obtained a substance which gave the reactions of xanthine. Only 0.16 gram was obtained by the author from 40 c.c. of dry hydrogen cyanide, and this gave the reactions described by Gautier, but did not yield murexide when the residue obtained by evaporating with chlorine water was moistened with ammonia. Since a mixture of the compound with one-tenth of its weight of xanthine gave this murexide reaction distinctly, it follows that the substance obtained from hydrogen cyanide was not xanthine.

A. H.

The Alkylates of Papaverine. By ADOLPH CLAUS and OSKAR KASSNER (*J. pr. Chem.*, 1897, [ii], 56, 321—345. Compare Abstr., 1893, i, 489).—When papaverine propobromide, C₂₀H₂₁NO₄·CH₂EtBr, is decomposed by aqueous alkalis, yellow masses separate if the

alkali is not too dilute; these dissolve in ether, and on evaporating the solution a yellow oil is obtained. This is *propylidenepapaverinium*, $C_{20}H_{21}O_4:N:CH_2Et$; it is insoluble in water, but in contact with it, or even when dissolved in moist ether, it is slowly converted into *propyl-papaverinium hydroxide*, $C_{20}H_{21}O_4:N(OH)\cdot CH_2Et$. This dissolves in water, imparting to it an alkaline reaction, and it is also soluble in moist ether; by the addition of plenty of dry ether to the latter solution, it can be obtained in unstable, colourless crystals. The presence of but a trace of alkali is sufficient to transform it into the yellow propylidenepapaverinium. In the presence of alcohol, it loses its alkaline reaction, becoming converted into *propylpapaverinium ethoxide*, $C_{20}H_{21}O_4:N(OEt)\cdot CH_2Et$; this is also formed when the yellow base is dissolved in alcohol, or when an alcoholic solution of papaverine propo-sulphate or propochromate is decomposed with lead hydroxide, and it can be obtained in colourless crystals, which melt at 137° , by adding ether to the alcoholic solution; its character is rather that of a salt. All the three substances described are converted by hydrogen chloride or hydrochloric acid into yellow *papaverine propo-chloride*, $C_{20}H_{21}O_4:NCl\cdot CH_2Et$, which melts at 80° .

Papaverine ethobromide and methiodide appear to yield each a similar series of compounds, but the reactions are less easy to study than in the case of the propyl derivatives. The benzochloride is even more readily converted by alkalis into *benzylidenepapaverinium*, $C_{10}H_{21}O_4:N:CHPh$, and this was obtained in yellow needles melting at about 130° ; when its ethereal alcoholic solution is allowed to evaporate spontaneously in the air, oxidation takes place and colourless crystals are obtained of a neutral substance which melts at 165° and appears to have the molecular formula, $C_{14}H_{15}NO_3$.

In the course of attempts to obtain papaverinium hydroxides, a few dichromates, $[C_{20}H_{21}O_4:N(CH_2R)]_2Cr_2O_7$, and sulphates, $[C_{20}H_{21}O_4:N(CH_2R)]_2SO_4$, were prepared; these were the yellow *benzochromate*, reddish-brown *ethochromate* melting at 139° , hygroscopic *methosulphate* melting at about 110° , and *propo-sulphate* which melts at 126° and crystallises with $2H_2O$.

Just as papaverine is converted into papaveroline by heating with hydriodic acid, [four methoxy-groups being exchanged for hydroxyl, so the alko-haloids of papaverine, $C_{20}H_{21}O_4:NX\cdot CH_2R$ [$R = H, Me, Et, Ph$; $X = Cl, Br, I$], yield the corresponding derivatives of papaveroline, $C_{16}H_{13}O_4:NX\cdot CH_2R$, the alko-chlorides when heated with hydrochloric acid at $160-180^\circ$, the alko-bromides with hydrobromic acid at $130-140^\circ$, and the hydriodides with hydriodic acid (and a little amorphous phosphorus) at 130° . In this way, the following derivatives of *papaveroline* were prepared (the numbers given are melting points). *Benzochloride*, 158° ; *methochloride*, 235° ; *ethochloride*, 215° , these are greenish; *propobromide*, 140° , yellowish; methiodide, 77° , reddish-brown.

C. F. B.

A New Alkaloid from Retama Sphaerocarpa. By J. A. BATTANDIER and TH. MALOSSE (*Compt. rend.*, 1897, 125, 360—362; see also this vol., i, 52).—The authors have extracted from the young shoots and bark of *Retama sphaerocarpa* a new alkaloid, *retamine*,

which they regard as a hydroxysparteine, $C_{15}H_{26}N_2O$; it differs, however, from all the known artificial hydroxysparteines. It crystallises from light petroleum in long needles melting and decomposing at 162° . It is sparingly soluble in water or ether, but dissolves readily in alcohol or light petroleum; when obtained by spontaneous evaporation from its alcoholic solution, it forms large, rectangular plates. The alkaloid colours phenolphthalein, and is a strong base, forming a series of well-defined salts; these salts contain either one or two molecules of a monobasic acid to one molecule of the alkaloid. The salts are decomposed by caustic potash or by large quantities of ammonia, but the base itself is sufficiently strong to decompose ammonium salts, and it also precipitates ferric and cupric hydroxides from solutions of these metals. It has strong reducing properties, is dextrogyrate, yields no precipitate with platinic chloride, and gives a feeble sparteine reaction with ammonium sulphide. J. J. S.

New Bile Pigments. By A. DASTRE and N. FLORESCO (*Compt. rend.*, 1897, 125, 581—583).—In addition to bilirubin, which the authors call the original pigment, and biliverdin, which they call the definite or final pigment, the biles of many animals contain two others which they call *biliprasinic* or *intermediate pigments*. Biliprasinic-yellow exists in the bile of the calf and in other yellow biles; it is changed to green (biliprasinic-green) by the action of carbonic anhydride, glacial acetic acid, and other acids, especially in presence of alcohol, is unstable in a vacuum, and is decomposed by light. Biliprasinic-green exists in the fresh bile of the ox, the rabbit, and other animals. Alkalis convert it into biliprasinic-yellow, this being the alkaline pigment, whilst the green is the acid pigment. In a vacuum, it changes into bilirubin. The characteristic difference between the biliprasinic pigments on the one hand, and bilirubin and biliverdin on the other, is that the biliprasinic acid is displaced from its combination with alkalis by carbonic anhydride, whilst bilirubin and biliverdin displace carbonic acid. All the pigments are derived from bilirubin by oxidation and hydration, and the biliprasinic acid is intermediate between it and biliverdin. The chief agents in bringing about these changes, except that of biliprasinic-yellow into biliprasinic-green or *vice versa*, are oxygen, which is indispensable, heat, light, and alkalis and acids. Marked alkalinity increases the stability of bilirubin, neutrality or acidity accelerates the formation of biliprasinic-green. Heat tends to change bilirubin into biliprasinic-green, and the latter into biliverdin, but prolonged heating at 100° decomposes the bilirubinate. Light rapidly converts bilirubin into biliprasin, and the latter into biliverdin. It is probable that the oxidation and hydration of bilirubin begins in the hepatic cellules and the biliary canaliculi; in all cases, these changes continue in the gall-bladder. The artificial conditions of the transformation are not realised in the animal body, and it is necessary to assume the existence of a particular oxidising agent, or a particular condition in the organism, occurring in the liver, and passing in part into the bile. C. H. B.

Organic Chemistry.

The Relation of Electrochemistry to Organic Chemistry. By KARL ELBS (*Zeit. Elektrochem.*, 1897, 4, 81—89).—An historical account is given of the researches of Kolbe, Kekulé, Crum Brown and Walker, von Miller and Mulliken and Weems on the electrolysis of salts of organic acids, and the connection between the conductivity of solutions of organic acids and their constitution and basicity is mentioned. Electrolytic reduction and oxidation processes are then considered, the researches of Goppelsroder, Gattermann, and Clement and Noyes being described. Of interest is the production of naphthazarine by the electrolytic reduction of 1:2' or 1:4'-dinitronaphthalene dissolved in sulphuric acid. By the electrolytic oxidation of paranitrotoluene, paranitrobenzylic alcohol may be prepared, a result not attainable by any chemical oxidising agent. The electrolytic product, ammonium persulphate, possesses specialised oxidising properties which are not found in any other oxidising agent; by its means orthonitrophenol and salicylic acid may be oxidised directly to nitroquinol and to quinolcarboxylic acid respectively, whilst anthraquinone is oxidised to alizarin, and alizarin to alizarin-bordeaux and alizarin-cyanine.

T. E.

[The Number of Isomeric Paraffins.] By F. HERRMANN (*Ber.*, 1898, 31, 91).—A reply to Losanitsch (this vol., i, 165).

Decomposition of Hexane and Trimethylethylene by Heat. By FRITZ HABER and H. OECHELHÄUSER (*Chem. Centr.*, 1897, i, 86, 225—226; from *J. Gasbel.*, 39, 799—805, 813—818, 830—834).—In continuation of the work of Haber and Samoylowicz (*Abstr.*, 1897, i, 307—308), the authors have investigated the decomposition of these gases at 900—1000° by passing them through a porcelain tube encased in a tube of platinum, platinum-iridium, or carbon which was heated electrically, the temperatures being measured by means of Le Chatelier's couple.

At 900—1000°, hexane is decomposed, yielding 29.22 per cent. of tar, 27.77 of methane, 22.14 of olefines, 6.76 (to 10) of benzene, 3.27 of carbon, 2.44 of hydrogen, and 1.1 of acetylene; the last four products probably result from bye-reactions. Only a small quantity of naphthalene was detected. The tar consists probably of a condensation product of the olefines, since it chars on nitration. In comparison with the decomposition at lower temperatures, more acetylene and benzene are formed, but the smaller quantity of olefines produced causes, on the whole, a diminution in the illuminating value of the gas. The authors now fix the limit to which hexane may be heated without producing much carbon and hydrogen at 940°.

The decomposition products obtained by heating trimethylethylene at 668—790° are similar to those obtained from hexane, and only a little carbon and hydrogen are formed. The tar, however, contains olefines with higher molecular weights than trimethylethylene; this is due to the instability of the primary decomposition products, which

have higher molecular weights than those obtained from hexane, and combine to form more complex compounds. The absence of any higher paraffins in the tar is also remarkable. Trimethylethylene when heated at $933-938^{\circ}$, forms a light brown vapour, which has the odour of naphthalene, the products of decomposition being 27.72 per cent. of methane, 8.10 of ethylene, 1.76 of hydrogen, 4.46 of gaseous by-products, 0.30 of acetylene, 5.09 of carbon, 8.00 to 13.41 of benzene, and 33.71 to 39.12 of tar. The quantity of benzene formed is greater than at lower temperatures, just as in the case of hexane, and, similarly, more methane is produced than corresponds with the removal of 1 mol. from 1 mol. of the original substance. The formation of benzene must depend on an initial production of acetylene, for hexane and trimethylethylene do not contain any long carbon chain in common. Trimethylethylene, when heated at $1050-1060^{\circ}$, is decomposed largely into carbon and naphthalene, hence at temperatures over 950° only complicated secondary actions take place.

Benzene, when heated at 900° , remains practically unchanged, but decomposes between 900° and 1000° , forming higher aromatic compounds, which are different, however, from those present in the tar obtained from hexane and trimethylethylene at these temperatures, and must result, therefore, from the combination of benzene with other compounds, especially acetylene. Diphenyl and a crystalline substance boiling at above 254° were found in the decomposition products of benzene, but neither naphthalene nor styrene was present, and only a small quantity of acetylene.

Acetylene when heated at $600-800^{\circ}$ forms a tar very rich in benzene, but containing only small quantities of aliphatic compounds. No flash of light was produced by the decomposition, as Lewes observed, except when air was present in the gas. E. W. W.

Laboratory Apparatus for preparing Gas from Light Petroleum. By PIETRO BARTOLOTTI (*Gazzetta*, 1897, 27, ii, 335-347).—The author has devised an apparatus for preparing heating or illuminating gas from light petroleum; it consists of two gasometers, connected with a carburetting cylinder filled with wood-wool, kept saturated with light petroleum, which saturates air passing through the carburetter. The air saturated with petroleum is drawn off to be burnt; in order to prevent firing back, a plug of wire gauze is used. W. J. P.

Recent Developments in Gas Lighting. By HANS BUNTE (*Ber.*, 1898, 31, 5-25).—An address delivered before the German Chemical Society. In the manufacture of coal-gas, the chief advance consists in the substitution of gaseous fuel for direct-heating, and the introduction of sloping instead of horizontal retorts. In Germany, notably in Westphalia and Silesia, large quantities of coal are carbonised for the sake of the coke, tar, and ammonia; a large quantity of benzene is obtained from the gases of these coke-furnaces, and the price of benzene has been so lowered thereby that it is extensively used for carburetting, and increasing the luminosity of coal gas; in this way, it is possible to obviate the necessity of mixing expensive coals, such as cannel and boghead, with coal which otherwise would give a gas of poor illuminating power. In America, illuminating gas is made largely by mixing

the vapour of low-boiling petroleum, or the decomposition products of the high-boiling fractions, with water-gas; this process is also being adopted in countries where these petroleum residues are to be had cheap, as in England, Belgium, Holland, and Denmark.

F. Siemens increased the amount of luminosity obtainable from coal-gas by means of a regenerative burner, in which the air supplied to the burner underwent a preliminary heating; a greater improvement was effected by the incandescent burner of Auer von Welsbach, in which a mantle of metallic oxides is heated to incandescence by a mixture of coal gas and air, burning underneath with a non-luminous flame. The mantles are woven of cotton gauze, and are impregnated with a mixture of thorium and cerium nitrates, dried, and eventually ignited; they contain 98—99 per cent. of thorium oxide, and 1—2 per cent. of cerium oxide; these are the most favourable proportions for luminosity: mantles of pure thorium oxide or pure cerium oxide give hardly any light at all. Experiments made by the author have shown that this mixture has no specially great emissive power for light rays; it, and the pure oxides, as well as carbon and magnesia, appear almost equally luminous when heated to the same high temperature. The explanation is to be sought in the catalytic action of cerium oxide, which lowers the kindling temperature of a mixture of hydrogen and oxygen from 650° to 350° . The mixture of air with the partly burned coal-gas rising from the burner at the foot of the mantle (a bunsen burner only sucks in about half the air needed to burn the gas completely) impinges on the particles of cerium oxide, and is brought by the action of the latter into extremely vigorous combustion; the great heat generated in this combustion makes the particles incandescent. Thorium oxide has no such catalytic action, and in consequence its presence might be thought prejudicial. The use it serves is in separating the particles of cerium oxide, for it is very voluminous when prepared by heating the nitrate. Cerium oxide, on the other hand, is fairly compact when so prepared, and a mantle made of it alone is but feebly luminous; this is probably because the heat is conducted away too fast, and the temperature never rises to that necessary for incandescence. The objection that the quantity of cerium oxide in a mantle is too small to produce so great a light is met by an approximate calculation, in which it is shown that the weight of cerium oxide in an incandescent burner of 70 candle power is about 4 milligrams, whilst the weight of incandescent carbon, present at any moment, in a luminous gas-flame of 20 candle power is about 0.1 milligram.

Mention is also made of acetylene as a source of light; it has found no extensive use as yet, because it is liable to explode when kept under pressure, or when subjected to a comparatively slight rise of temperature, and because of its great range of explosibility when mixed with air, any mixture containing between 5 and 80 per cent. of acetylene being explosive. In other respects, acetylene has great advantages; the calcium carbide, from which it is prepared by the action of water, contains more light-giving power condensed in a given space than any other substance. A passing reference is made to the lighting of railway carriages by means of oil-gas (made from paraffin oil), alone or mixed with acetylene.

In spite of the introduction of electric lighting, the consumption of coal-gas in Germany has progressed at an increasing rate. With regard to efficiency and economy of lighting, the following table is interesting.

	Coal gas.					Acetylene.	Petroleum.	Spirit (Incandescent).	Electric (Incandescent).
	Ordinary burner.	Regenerative burner.	Incandescent.						
			Old form.	New form.	With compressed gas.				
Candle power per 10 cub. ft. per hour	33	64	142	170	283	437	94*	94*	...
20 candle power costs per hour	2·8 <i>d.</i>	1·6 <i>d.</i>	0·75 <i>d.</i>	0·62 <i>d.</i>	0·37 <i>d.</i>	1·91 <i>d.</i>	1·8 <i>d.</i>	2·1 <i>d.</i>	5·3 <i>d.</i>

* Per kilo. per hour.

C. F. B.

Electrolytic Preparation of Iodoform. By KARL ELBS and A. HERZ (*Zeit. Elektrochem.*, 1897, 4, 113—118. Compare Foerster and Meves, this vol., i, 166).—Solutions containing alcohol, sodium carbonate, and potassium iodide are placed in a porous cell containing an anode of platinum gauze; the cell stands in a solution of sodium carbonate, in which the nickel gauze cathode is immersed. The theoretical yield of iodoform should be 1·468 grams per ampère hour, but in practice some iodic acid and small quantities of organic iodine compounds other than iodoform are produced. The best yield of iodoform is obtained at from 60—70°; the amount of iodic acid formed also increases slightly with the temperature. An increase in the concentration of the sodium carbonate solution slightly diminishes the yield of iodoform and considerably increases the formation of iodate, whilst an increase in the concentration of the iodide or of the alcohol has the opposite effects. This is to be expected, because the greater the concentration of the carbonate the greater is the amount of oxygen liberated at the anode, whereas an increase in the amount of iodide will increase the relative quantity of iodine liberated, and a greater concentration of alcohol will provide a better opportunity for the iodine to react with it. With an anode solution containing 6 grams of sodium carbonate, 10 grams of potassium iodide, 20 c.c. of 96 per cent. alcohol, and 100 c.c. of water, the best results were obtained with a current density of 0·5 to 1 ampère per sq. dcm. of anode surface. The yield increases as the process is continued, provided the composition of the solution is maintained constant. A solution of the above composition, except that 5 instead of 6 grams of sodium carbonate were used, gave at 60°, with a current density at the anode not exceeding 1 ampère per sq. dcm., over 97 per cent. of the theoretical yield of iodoform. The diaphragm may be omitted if a small cathode, placed near the surface of the solution, is employed.

The iodoform produced is perfectly pure. When acetone is used in place of alcohol, very little iodoform is obtained, the product consisting mainly of iodoketones and condensation products of acetone. Attempts to prepare bromoform and chloroform in the way used for iodoform gave negative results.

T. E.

Bromine Derivatives of 2:3-Dimethylbutane. By HENRY L. WHEELER (*Amer. Chem. J.*, 1898, 20, 148—153).—2:3-Dibromo-2:3-dimethylbutane, prepared from pinacone by the methods of Baeyer (Abstr., 1894, i, 45) and of Thiele (Abstr., 1894, i, 217), melts at 192°. When 1 molecular proportion of bromine is added to this in presence of iron wire, no tribromo-derivative is obtained, but 1:2:3:4-*tetra-bromo-2:3-dimethylbutane*, $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CMeBr}\cdot\text{CH}_2\text{Br}$, is immediately formed; this melts at 139°, and is also formed on adding bromine to the 2:3-dimethyl-1:3-butadiene obtained by the action of alcoholic potash on 2:3-dibromo-2:3-dimethylbutane.

When isobutylic bromide is heated with bromine in presence of iron wire, 1:2-dibromo-2-methylpropane is formed, although the yield is poor; Linnemann (Abstr., 1872, 478) states that he was unable by direct bromination to detect the formation of this compound.

W. A. D.

Regularities in the Boiling-points of Isomeric Aliphatic Compounds. By ALEXANDER NAUMANN (*Ber.*, 1898, 31, 30).—The author had long anticipated Menshutkin (this vol., i, 116) in noting these regularities (compare *Thermochemie*, p. 167; and this Journal, 1874, 529, 563).

C. F. B.

Chemistry of Whiskey. By ALFRED H. ALLEN (*J. Fed. Inst. Brew.*, 1897, 3, 24—46).—An account is given of the manufacture of whiskey, and of the nature of its secondary constituents (higher alcohols, ethereal salts, &c.). The author finds that if spirit containing amylic alcohol is allowed to remain for some time in contact with oak or cork shavings, a large proportion of the amylic alcohol will be absorbed by the shavings, and he attributes the well-known effect of storing whiskey in oaken casks partly to this selective absorption. Analyses are given of the spirituous liquid obtained by steaming old whiskey casks; this is found to be very much richer in both fusel oil and ethers than whiskey itself.

A. C. C.

Volatile Bye-products of Fermentation. By ALFRED C. CHAPMAN (*J. Fed. Inst. Brew.*, 1897, 3, 240—254).—An account is given of the better known volatile fermentation bye-products, and the manner in which they are formed is discussed. It is found that there is but little difference between the amounts of higher alcohols formed during the earlier and later stages of fermentation, and further that the quantities of these alcohols present in samples of beer which had been stored for more than twenty years were not sensibly greater than are usually found in recently made beers. These results are opposed to Lindet's supposition that these substances are not products of the normal fermentation of sugar, but that they are only formed under abnormal conditions of yeast life, consequent on the disappearance of the fermentable sugar. In an attempt to separate the ethereal salts

present in old beer, ethylic acetate and ethylic butyrate were identified. When fresh malt-wort is distilled, furfuraldehyde is always present in the distillate. An approximate estimation of the amount of this substance in the wort and also in the resulting beer showed that little, if any, had been formed during fermentation; it is therefore an unfermented wort constituent, and not a product of fermentation. Analyses are given showing the amounts of ethereal salts, higher alcohols, furfuraldehyde and acetaldehyde present in five samples of English beers; the effect of storage on the amounts of the above constituents was investigated, and analyses are given showing the quantities present in three samples of beer which had been in bottle from sixteen to twenty years.

Numbers are given showing the effects of high and low fermentation temperatures on the production of ethereal salts and higher alcohols; at the higher temperatures, increased quantities of both of these constituents are formed. Details are also given of the methods adopted for the estimation of the bye-products referred to in the paper.

A. C. C.

Action of Zinc on Monochloromethylic Ether. By MICHELE FILETI and AUSONIO DE GASPARI (*Gazzetta*, 1897, 27, ii, 293—296).—No reaction occurs on boiling monochloromethylic ether with anhydrous zinc chloride, but on heating the ether with zinc, a violent reaction occurs, methylic chloride, zinc chloride, hydrogen chloride, methylal, and methylic-2-chlorethylic ether being produced.

Methylic 2-chlorethylic ether, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OMe}$, when isolated by fractional distillation, is a colourless liquid, heavier than water; it boils at $90\text{--}91^\circ$ under 735.7 mm. pressure, and has the normal vapour density by V. Meyer's method at the temperature of boiling xylene. It does not fume in the air, thus contrasting with methylic 1-chlorethylic ether and chloromethylic ethylic ether (Favre, *Abstr.*, 1895, i, 14); it is probably produced by a reaction represented by the equation, $\text{CH}_2\text{Cl}\cdot\text{OMe} + \text{CH}_3\text{Cl} = \text{HCl} + \text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OMe}$, and is not affected by boiling with sodium, zinc, or zinc chloride, or by heating with sodium acetate or silver at 150° .

W. J. P.

Chloromethylic Ethylic Ether. By AUSONIO DE GASPARI (*Gazzetta*, 1897, 27, ii, 297—298).—The author has prepared chloromethylic ethylic ether, $\text{CH}_2\text{Cl}\cdot\text{OEt}$ (compare Favre, *Abstr.*, 1895, i, 14), by saturating a mixture of aqueous formaldehyde and ethylic alcohol with hydrogen chloride in a freezing mixture, separating the upper layer of liquid and subjecting it to fractional distillation; it boils at $79\text{--}80^\circ$, with slight evolution of hydrogen chloride, and is readily decomposed by water. On treating it with anhydrous sodium acetate, reaction takes place easily, the *acetate*, $\text{EtO}\cdot\text{CH}_2\cdot\text{OAc}$, being formed; this is an oil of pleasant odour, is heavier than water, and boils at $130\text{--}131^\circ$ under 738.6 mm. pressure.

W. J. P.

Neutralisation of Glycerophosphoric Acid in Presence of Helianthin A and Phenolphthalein. By H. IMBERT and A. ASTRUC (*Compt. rend.*, 1897, 125, 1039—1040).—Glycerophosphoric acid is acid to both helianthin A and to phenolphthalein. When neutralised with an alkali, it behaves as a monobasic acid in presence

of the former and as a dibasic acid in presence of the latter. The radicle, $\text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, has affected only the alcoholic function of the phosphoric acid, and is without influence on either of the true acidic functions.

C. H. B.

Aliphatic Nitroso-compounds. By OSCAR PILOTY (*Ber.*, 1898, 31, 218—220).—Victor Meyer, as the result of his researches on the action of nitrous acid on various aliphatic compounds (*Abstr.*, 1888, 702) came to the conclusion that true nitroso-compounds are rarely if ever met with in the aliphatic series. The product obtained by Baeyer by the union of nitrosyl chloride with terpineol acetate (*Abstr.*, 1894, i, 252), and by Thiele by the union of the same substance with tetramethylethylene (*ibid.*, i, 217) are undoubtedly to be regarded as true nitroso-derivatives, as also are Meyer's pseudo-nitroles. From these results, and from experiments previously conducted by the author on the action of benzenesulphonic chloride and alkali on hydroxylamine derivatives (*Abstr.*, 1896, i, 555), the conclusion is drawn that only such compounds are capable of yielding true nitroso-derivatives which contain nitrogen attached to a tertiary carbon atom. The author has succeeded in obtaining aliphatic nitroso-derivatives from compounds containing the hydroxylamido- or nitro-groups attached to a tertiary carbon atom (see following abstract). All these nitroso-compounds are colourless in the solid state but give deep blue solutions.

J. J. S.

Aliphatic Nitroso-compounds. By OSCAR PILOTY and OTTO RUFF (*Ber.*, 1898, 31, 221—225. Compare preceding abstract).—When tertiary nitro-alcohols are reduced, or tertiary hydroxylamine derivatives are oxidised, a deep blue solution is always obtained and this probably contains the nitroso-compound; in no case, however, could such a compound be isolated. Aliphatic nitroso-compounds can readily be obtained by the oxidation of acetyl derivatives of tertiary hydroxylamido-alcohols with chromic anhydride. The compounds thus obtained are colourless but give deep blue solutions, and even fuse to blue liquids; they are volatile; their vapours have an odour of mustard oil and they give Liebermann's nitroso-colour reaction.

Tertiary triacetylnitroisobutylglycerol (triacetylmethylol-2-nitro-2-propandiol-1:3), $\text{NO}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{OAc})_3$, is obtained when nitroisobutylglycerol (*Abstr.*, 1897, i, 4) is heated with three times its weight of acetic anhydride on the water bath and then boiled for $\frac{1}{4}$ hour; it crystallises from 95 per cent. alcohol in hard, rhombic prisms, melts at $74-75^\circ$, is only sparingly soluble in water or light petroleum, but dissolves more readily in ether, hot alcohol, acetic acid, or benzene. When it is reduced in ethereal solution with aluminium amalgam and water, *triacetyliso-butyl- β -hydroxylamine* (triacetylmethylol-2-hydroxylamino-2-propandiol-1:3), $\text{OH} \cdot \text{NH} \cdot \text{C}(\text{CH}_2 \cdot \text{OAc})_3$, is formed, and is best isolated in the form of its *oxalate*, $\text{C}_{12}\text{H}_{19}\text{NO}_{11} + \frac{1}{2}\text{H}_2\text{O}$, which crystallises from ethylic acetate in slender needles melting and decomposing at 95° ; it dissolves readily in water and alcohol, but is only sparingly soluble in ethylic acetate and ether. *Nitrosotriacetyliso-butylglycerol*, $\text{NO} \cdot \text{C}(\text{CH}_2 \cdot \text{OAc})_3$, is obtained when the crude ethereal solution of the hydroxylamine derivative (from 10 grams of the nitro-compound) together with the

aluminium hydroxide is cooled to 0° and then oxidised with an ice-cold solution of potassium dichromate (3 grams) and concentrated sulphuric acid (5 c.c.) in water (300 c.c.); the mixture is well shaken for a few minutes in a separating funnel, the deep blue ethereal solution separated, washed 2—3 times with water, and the ether distilled; the residue, after recrystallisation from methylic alcohol, forms needles melting at 73° (corr.). It is sparingly soluble in water, readily in hot alcohol and moderately in benzene or acetic acid, and is decomposed when warmed with hydrochloric acid, yielding acetic acid, formaldehyde, and an amorphous compound.

Tertiarydiacetylnitropentandiol, $\text{NO}_2 \cdot \text{CEt}(\text{CH}_2 \cdot \text{OAc})_2$, obtained from Pauwel's nitropentandiol, is a thick, colourless, odourless syrup boiling at 168° under a pressure of 22 mm.; it is practically insoluble in water but is readily miscible with alcohol or ether. *Diacetylnitrosopentandiol*, $\text{NO} \cdot \text{CEt}(\text{CH}_2 \cdot \text{OAc})_2$, crystallises from light petroleum in glistening, prismatic plates, melts at $71\text{--}72^{\circ}$ (corr.) is sparingly soluble in benzene or ethylic acetate, and in odour resembles nitrosobenzene. *Diacetylnitrobutandiol*, $\text{NO}_2 \cdot \text{CMe}(\text{CH}_2 \cdot \text{OAc})_2$, crystallises in compact needles, melts at $27\text{--}28^{\circ}$, and distils at 158° under a pressure of 20 mm., it is readily soluble in ether or alcohol, sparingly in light petroleum, and almost insoluble in water. The corresponding *nitroso*-compound $\text{NO} \cdot \text{CMe}(\text{CH}_2 \cdot \text{OAc})_2$, melts at 53° (corr.), is readily soluble in alcohol or ether, but only sparingly in light petroleum. J. J. S.

Action of Benzhydrazide on Glucose. By GEORG PINKUS (*Ber.*, 1898, 31, 31—37).—The product described by Davidis as glucosebenzosazone, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot [\text{C}(\text{N} \cdot \text{NHBz})]_3 \cdot \text{CH} \cdot \text{N} \cdot \text{NHBz}$ (*Abstr.*, 1897, i, 5), and obtained by heating glucose with benzhydrazide and very dilute caustic soda for $1\frac{1}{2}$ hours on the water bath, is shown to be a mixture of the benzosazones of glyoxal and methylglyoxal. When it is extracted repeatedly with large quantities of boiling alcohol, *glyoxal benzosazone*, $\text{C}_2\text{H}_2(\text{N} \cdot \text{NHBz})_2$, is left; an identical product is obtained from glyoxal and benzhydrazide; it decomposes at about 380° . The hot alcoholic extract deposits *methylglyoxalbenzosazone*, $\text{C}_2\text{HMe}(\text{N} \cdot \text{NHBz})_2$, on cooling; an identical product is obtained from benzhydrazide and either glycerose or methylglyoxal; it melts and decomposes at $251\text{--}252^{\circ}$. This substance is converted by heating with phenylhydrazine into methylglyoxal phenylosazone melting at 148° , which is also obtained when glucose is heated with phenylhydrazine and very dilute caustic soda.

It is not probable that the methylglyoxal is derived from glyceric aldehyde, which would be a primary product of the decomposition of glucose, for although this aldehyde (glycerose: see above) reacts with benzhydrazide in weak acetic acid solution, yielding methylglyoxal benzosazone, the reaction is extremely slow in alkaline solution. More probably, the methylglyoxal is derived from acetol, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OH}$, for this reacts with benzhydrazide in alkaline solution, yielding methylglyoxal benzosazone; with phenylhydrazine in acetic acid solution, it yields acetolphenylhydrazone (Laubmann, *Abstr.*, 1888, 366), which has now been obtained crystalline, and melts at $100\text{--}102^{\circ}$.

Methylglyoxal is formed from dihydroxyacetone (Piloty, this vol., i,

117), when the latter is distilled with dilute sulphuric acid, for the distillate yields methylglyoxal phenylosazone when it is treated with phenylhydrazine. C. F. B.

Action of Boiling Water on d-Fructose (Levulose). By CORNELIS ADRIAAN LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, 16, 282—283).—In order to ascertain whether any transformation occurs when sugars are heated with water alone, fructose was boiled with water in a platinum reflux apparatus for 80 hours. Beyond a slight diminution in the specific rotatory power of the fructose, no other change was observed. A. R. L.

Production and Occurrence of Levulose in Factory Products. By H. C. PRINSEN (*Bied. Centr.*, 1897, 26, 767—770; from *Arch. Java-Suikerind.*, 1896, Afl. 7).—In reply to Pellet, who states that levulose is precipitated by basic lead acetate (*Bull. Assoc. Chimistes*, 1896, 562), the author shows that lead acetate does not precipitate levulose. The rotatory power is slightly altered in alkaline solutions, but is restored by a drop of acetic acid. In presence of substances which are precipitated by basic lead acetate, the precipitate carries down the levulose; this occurs only when basic lead acetate is employed, and there is no precipitation of levulose with normal lead acetate in neutral or acid solutions. Dextrose is not precipitated.

With regard to factory products, which are usually neutral, polariscope results are not trustworthy. In molasses, levulose and dextrose are present in equal amounts, owing to changes during the processes of manufacture. Levulose could not be detected in ripe canes. In analysing such products, normal lead acetate should be employed, together with fine animal charcoal.

When a 10 per cent. dextrose solution is heated at 100° with sodium or potassium acetate (Na_2O or $\text{K}_2\text{O} = 2.5$ per cent.), the rotatory power is reduced to less than half in 4 hours, whilst the amount of reducing substance remains about the same. This explains the presence of levorotatory glucose in molasses originally dextrorotatory in the juice. (compare *Zeits. Ver. Rübenzuckerind.*, 1895, 320, and de Bruyn and Alberda van Ekenstein, *Abstr.*, 1896, i, 116). The results indicate that, in plants, the production of levulose from dextrose may be effected by salts of organic acids instead of by free bases as has been assumed. Ordinary cane-sugar molasses was found to contain, besides saccharose, dextrose and levulose in about equal amounts, and almost 5 per cent. of mannose. The mannose can only have been produced during the treatment in the factory. N. H. J. M.

Action of Alkalis on the Sugars. IV. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, 16, 257—261).—General remarks on the papers following.

A. R. L.

Action of Alkalis on the Sugars. V. Transformation of Galactose. The Tagatoses and Galtose. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, 16, 262—273).—When a 20 per cent. aqueous solution of galactose is

heated at 70° for 3 hours with 3 per cent. (on the sugar) of potassium hydroxide, the rotatory power sinks to $[\alpha]_D = +37.5^{\circ}$, and the solution contains about 50 per cent. of unaltered galactose, which can, for the most part, be removed by crystallisation. The residual syrup is mixed with a little methylic alcohol and extracted with acetone. On evaporating the solvent, a syrup is obtained containing a little galactose, and other reducing sugars, namely, *d*-tagatose, ψ -tagatose, galatose, and *d*-talose. The galactose is precipitated as methylphenylhydrazone, or is removed by fermentation with yeast.

d-Tagatose, $C_6H_{12}O_6$, crystallises from water and melts at 124° . The specific rotatory power is $[\alpha]_D = +1^{\circ}$, and this becomes -2.6° at 60° . Like fructose, it is decomposed by dilute acids, and gives an intense reddish-violet coloration with hydrochloric acid and resorcinol; it is unfermentable with yeast. When treated with alkalis, about 10 per cent. is transformed into galactose. It forms an amorphous compound with acetone (2 mols.), which has a rotatory power of $[\alpha]_D = +50^{\circ}$ (about). The *osazone* melts at 193° , and its solutions are optically inactive.

ψ -Tagatose, $C_6H_{12}O_6$, separates from water, in which it is less soluble than *d*-tagatose, in well-defined crystals which melt at 156° . The specific rotatory power of a 2 per cent. and 6 per cent. solution is $[\alpha]_D = +33.4^{\circ}$ and $+35^{\circ}$ respectively, and these values remain unaltered when the temperature is raised to 60° . The aqueous solution is perceptibly sweet. Its behaviour towards dilute acids and with hydrochloric acid and resorcinol is the same as that of *d*-tagatose, but it is slowly fermentable with yeast. When treated with alkalis, about 14 per cent. is transformed into galactose. The *osazone* melts at 140° , dissolves in 333 parts of boiling water, and its solution in acetic acid has a rotatory power of $[\alpha]_D = +21^{\circ}$.

Both *d*- and ψ -tagatose resemble fructose in their indifference towards iodine and bromine; the authors did not succeed in preparing acetyl derivatives from these sugars.

Galatose, $C_6H_{12}O_6$, is present in the mother liquor from which the sugars just described are isolated, but is best prepared by heating a 20 per cent. solution of galactose with lead hydroxide (10 per cent. on the sugar). After removing the lead salts, first with alcohol and then by precipitation with an alcoholic solution of tartaric acid, the galactose is eliminated by fermentation with yeast; a syrup is finally obtained consisting of galatose with a little *d*-talose. Galatose, which has not yet been obtained in a crystalline form, is unfermentable with yeast, optically inactive, and has an indistinctly sweet taste. It yields acids, but no galactose, when treated with alkalis. The *osazone* is soluble in 500 parts of boiling water, and melts at 182° ; the rotatory power of a solution in methylic alcohol is $[\alpha]_{Auer} = +19^{\circ}$. The sugar, like the ketoses, is unstable towards dilute acids, but its reducing power towards Fehling's and Romijn's (iodine) solution is about half that of the better-known aldoses. It yields about 4—5 per cent. of furfuraldehyde when distilled with hydrochloric acid.

d-Talose is only formed in these transformations in very small amount (at most 8 per cent.), and although it can be precipitated as the naphthylhydrazone, or 1 : 4-nitrophenylhydrazone, the precipitation is incomplete. Talose mixed with organic acids may be prepared by

decomposing the other sugars in the transformation products by means of acids. The authors have not, therefore, succeeded in crystallising talose.
A. R. L.

Action of Alkalis on the Sugars. VI. Glucose and ψ -Fructose.
By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, **16**, 274—281).—Glucose, $C_6H_{12}O_6$, is invariably formed when the three sugars, glucose, mannose, and fructose are transformed reciprocally into one another. It is best prepared by heating a 20 per cent. solution of fructose at 100° with lead hydroxide (10 per cent. on the sugar). After removing the lead salt, the product is fermented with yeast, when glucose remains in the form of a syrup; the authors have not yet succeeded in obtaining it in a crystalline form. It is optically inactive, and in this and several other properties resembles galactose (preceding abstract); the *osazone*, however, is soluble in 200 parts of boiling water, melts at 165° , and a solution in methylic alcohol has a rotatory power of $[\alpha]_{Auer} = +6^\circ$.

There is some evidence that when glucose, mannose, or fructose is heated with alkali hydroxides, a fifth sugar, a ketose, which may be denoted ψ -fructose, is present among the products. Thus, if an attempt be made to estimate the fructose in the mixture of sugars, it would appear that the sugar present has a lower laevorotation than ordinary fructose, and this is also confirmed by directly observing the rotatory power of the supposed fructose regenerated from the insoluble lime compound obtained from the same mixture. The view that ψ -fructose is present is also supported by the fact that the authors have isolated a new *osazone* from the mixture, which melts at 160° and, when dissolved in methylic alcohol, has a rotatory power of $[\alpha]_{Auer} = -5.3^\circ$.

The authors have previously drawn attention to the occurrence of mannose in the molasses obtained from the products of the sugar cane, this sugar being formed by the action of lime, with which the cane juice is boiled, on the invert-sugar. They now show that such molasses contains also glucose, the amount of which may be approximately estimated by fermenting the molasses with yeast, and subsequently determining the reducing power of the residue before and after treatment with hydrochloric acid according to the Sieben-Dammüller method. In this way, a sample of Louisiana molasses was shown to contain 4.8 per cent. of glucose, whilst 2.6 per cent. of the same sugar was found in a sample of Egyptian molasses. The Louisiana molasses also contained 0.4 per cent. of mannose.
A. R. L.

Nitration of Carbohydrates. By WILHELM WILL and FRIEDRICH LENZE (*Ber.*, 1898, **31**, 68—90).—In order to throw light on the nature of the bye-products arising from the nitration of cellulose, the authors have investigated the behaviour of various carbohydrates towards a mixture of concentrated nitric and sulphuric acids, it having been observed that cellulose is resolved into sugar under the influence of dilute acids. The nitrates obtained by this means are readily oxidised by Fehling's solution, and rotate the plane of polarised light; they dissolve in acetone, acetic acid, and alcohol, but are insoluble in water and petroleum. They do not dissolve in cold, concentrated hydro-

chloric acid, and undergo decomposition when the liquid is heated, chlorine being set free; boiling water gradually decomposes them, eliminating oxides of nitrogen, with slow dissolution of the product.

Rhamnose tetranitrate, $C_6H_8O_5(NO_2)_4$, separates from alcohol in colourless, rhombic crystals and melts at 135° , decomposing at 136° ; a 2.3 per cent. solution in methylic alcohol has $[\alpha]_D = -68.4^\circ$.

Arabinose tetranitrate, $C_5H_6O_5(NO_2)_4$, is deposited by alcohol in monoclinic crystals and melts at 85° , decomposing at 120° ; a freshly prepared 4.4 per cent. solution in alcohol has $[\alpha]_D = -101.3^\circ$, which drops to -90° after 20 hours.

Xylose anhydride dinitrate, $C_5H_6O_4(NO_2)_2$, crystallises from alcohol in spherical aggregates and melts at $75-80^\circ$.

Glucose pentanitrate, $C_6H_7O_6(NO_2)_5$, is an amorphous powder which melts at 10° , decomposing at 135° ; it dissolves very readily in alcohol, and is insoluble in water and petroleum. In a 6 per cent. alcoholic solution, it has $[\alpha]_D = 98.7^\circ$; it reduces Fehling's solution when heated with it.

Galactose pentanitrate, $C_6H_7O_6(NO_2)_5$, occurs in two forms. The α -modification dissolves less readily in alcohol, from which it crystallises in slender, transparent needles, and melts at $115-116^\circ$, decomposing at 126° ; a 4 per cent. solution in alcohol has $[\alpha]_D = 124.7^\circ$. The β -compound crystallises in monoclinic needles, melts at $72-73^\circ$, and decomposes at 125° ; a 6.7 per cent. solution in alcohol has $[\alpha]_D = -57^\circ$.

Mannose pentanitrate crystallises from absolute alcohol in transparent, rhombic needles, melts at $81-82^\circ$, and decomposes at 124° ; a 5 per cent. solution has $[\alpha]_D = 93.3^\circ$.

Lævulosan trinitrate, $C_6H_7O_5(NO_2)_3$, is produced in two distinct forms. The α -modification crystallises from alcohol in lustrous needles, melts at $137-139^\circ$, and decomposes at 145° ; a 1 per cent. solution in methylic alcohol has $[\alpha]_D = +62^\circ$. The β -compound crystallises in spherical aggregates, melts at $48-52^\circ$, and decomposes at 135° ; a 5 per cent. solution in alcohol has $[\alpha]_D = 20^\circ$.

Sorbinosan trinitrate, $C_6H_7O_5(NO_2)_3$, melts indefinitely at $40-45^\circ$.

α -Glucoheptose hexanitrate, $C_7H_8O_7(NO_2)_6$, crystallises from alcohol in transparent needles and melts at 100° ; a 3.4 per cent. solution in alcohol has $[\alpha]_D = +104.8^\circ$.

α -Methylglucoside tetranitrate, $C_7H_{10}O_6(NO_2)_4$, crystallises from alcohol in lustrous, quadratic plates, melts at $49-50^\circ$, and decomposes at 135° ; a 6.2 per cent. solution in alcohol has $[\alpha]_D = 140^\circ$.

Methyl-d-mannoside tetranitrate crystallises from alcohol in slender needles resembling asbestos and melts at 36° ; a 2.5 per cent. solution in alcohol has $[\alpha]_D = 77^\circ$.

Succharose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallises in spherical aggregates, melts at $28-29^\circ$, and decomposes at 135° ; a 3.4 per cent. solution in alcohol has $[\alpha]_D = 52.2^\circ$.

Lactose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallises from alcohol in leaflets and melts at $145-146^\circ$; a 2.8 per cent. solution in methylic alcohol has $[\alpha]_D = 74.2^\circ$. This compound closely resembles the pentanitrate described by Gélis. The *hexanitrate* melts at 81° .

Maltose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallises from alcohol in

lustrous needles, and melts and decomposes at $163\text{--}164^\circ$; a 3.5 per cent. solution in glacial acetic acid has $[\alpha]_D = 128.6$.

Trehalose octonitrate crystallises from alcohol in nacreous leaflets, melts at 124° , and decomposes at 136° ; a 4 per cent. solution in glacial acetic acid has $[\alpha]_D = 173.8^\circ$.

Raffinose undecanitate, $C_{18}H_{21}O_{16}(NO_2)_{11}$, separates from alcohol in amorphous, spherical aggregates, melts indefinitely at $55\text{--}65^\circ$, and decomposes at 136° ; a 3.6 per cent. solution in alcohol has $[\alpha]_D = +94.9^\circ$.

β -*Glucosan trinitrate*, $C_6H_7O_3(NO_2)_3$, crystallises from alcohol in lustrous needles and melts at 101° ; a 2.4 per cent. solution in alcohol has $[\alpha]_D = -61.4^\circ$.

A hexanitro-derivative of starch, $C_{12}H_{14}O_{10}(NO_2)_6$, is an amorphous powder which decomposes at 194° without previously melting (compare Mühlhäuser, Abstr., 1893, i, 6).

Wood gum also yields a nitro-derivative (compare Bader, Abstr., 1896, i, 335).
M. O. F.

Carbohydrates contained in the Corm of Cyclamen Euro-pæum. By BOHUSLAV RAYMAN (*Chem. Centr.*, 1897, i, 230—231; from *Rozprawy české akademie*, 1896, Cl. 2, Nr. 30).—Cyclamose and cyclamin are obtained from the corm by extracting it with 70 per cent. alcohol, and may be separated by means of absolute alcohol in which the latter is soluble. *Cyclamin*, $C_{27}H_{38}O_{13}$, which is purified by precipitating it from a concentrated aqueous solution by ether, gives a dark red coloration with fuming sulphuric acid; the aqueous solution froths like that of saponin, but is more easily decomposed by acids or by boiling. By the action of sulphuric acid, it is decomposed into cyclam-iretin, $C_{14}H_{18}O_2$, levulose, and a dextrorotatory sugar, *cyclose*. *Cyclam-iretin* yields an amorphous bromine additive compound, a benzoate, and an acetate. Cyclamose, $C_{36}H_{62}O_{31}$, which the author proposes to name *cyclamosin*, is a white, amorphous powder, has a sweetish taste, deliquesces, and becomes black on exposure to the air, and with hydrochloric acid yields levulose.

No mannitol could be detected, and the residue left after extracting with alcohol consists of starch and cellulose.
E. W. W.

Pentosans in the Beet Sugar Manufacture. By K. KOMERS and ANTON STIFT (*Bied. Centr.*, 1897, 26, 861; from *Oesterr. Zeit. Zuckerind.*, 1897, 627).—In purifying beetroot sap in the usual manner, most of the pentosans are removed and are probably converted by the action of the lime into more or less complex, insoluble compounds which would be retained in the deposit. A part of the pentosans pass to the green syrup and from this to other products; only a slight amount is to be found in the molasses. A portion of the pentosans remains in the crude sugar and it is very likely that they form a not inconsiderable portion of the organic impurity present in crude sugar. The reducing action of many crude sugars is perhaps due in part to the presence of pentosans as well as to invert-sugar.
N. H. J. M.

The Conversion of Starch by means of Sulphurous Anhydride and Sulphurous Acid. By A. BERGÉ (*Bied. Centr.*, 1897, 26, 863; from *Zeit. Spir. Ind.*, 1897, 206).—Liquid sulphurous anhydride

converts dry starch first into soluble starch and then into dextrin when heated above 80° . Below this temperature, there is no action, whilst at temperatures slightly above 115° , soluble starch is the chief product. Sulphurous acid has no effect on starch below 45° ; at 100° , the starch dissolves, whilst at a temperature not above 115° (with 1 per cent. sulphurous acid) a gummy product is obtained consisting of a little soluble starch and dextrans with 5 to 10 per cent. of dextrose. At 135 — 140° , the starch is converted entirely into dextrose; this change is best effected by heating starch (25 per cent.) and 3—6 per cent. sulphurous acid (75 per cent.) for an hour at 140° .

N. H. J. M.

Precipitation of Carbohydrates by Neutral Salts. By ROBERT ARTHUR YOUNG (*J. Physiol.*, 1898, 22, 401—422).—The salt precipitation (salting out) method can be quite as easily applied to the separation of colloid carbohydrates as to proteids. Ammonium sulphate, magnesium sulphate, and sodium sulphate (at 33° , the temperature of its greatest solubility) are the most generally useful salts, but the crystalline carbohydrates cannot be precipitated by this method. Starch and soluble starch are both readily precipitable by salts. The erythro-dextrans are quite distinct from either starch or the achroodextrans, a fact entirely in opposition to the views of Musculus and Meyer and of Ost. Of these substances, two are precipitable by salts and one is not; these three substances, distinguished as erythrodextrin i, ii, and iii, give reactions closely similar to the products obtained by Lintner and Düll by other methods. The main bulk of the achroodextrans is not precipitable by this means. Glycogen is readily and completely precipitated by saturation with ammonium sulphate, or by sodium sulphate at 33° , and is thus readily distinguished from erythrodextrin iii. Inulin is partly precipitated from its solutions by salts, especially by magnesium sulphate. All the soluble iodine compounds of starch, soluble starch, and the erythro-dextrans are precipitated by salts more readily than the original carbohydrate. The colour of the iodine compounds varies with the concentration of the iodine. Soluble starch gives a blue coloration with iodine under all conditions, and has a greater attraction for iodine than the erythro-dextrans. Erythrodextrin i gives a reddish-purple with iodine after the removal of all soluble starch. There is no evidence as to the existence of a combination of the colloid precipitated and the salt precipitating, neither does the precipitating, or water-attracting, power of a salt depend on its molecular weight or its solubility.

W. D. H.

Hydrolysis of Glycogen. By M. CHRISTINE TEBB (*J. Physiol.*, 1898, 22, 423—432).—In the hydrolysis of glycogen, produced by mineral acids, intermediate substances of the dextrin class are formed which may be termed soluble glycogen, erythrodextrin, and achroodextrin. The final sugar formed is dextrose (identified by its osazone) and prolonged hydrolysis converts all the intermediate dextrans into sugar.

The intermediate dextrans may be separated by fractional precipitation with alcohol, and also by Young's salt saturation method (preceding abstract); this is a valuable means of discriminating between

erythrodextrin on the one hand, and glycogen and soluble glycogen on the other.

In the hydrolysis of glycogen, produced by the amylolytic enzymes of saliva, pancreatic extract, and malt extract, the only dextrans which could be separated in amount sufficient to work with subsequently are of the achroo-variety; small quantities of erythrodextrin were sometimes obtained, but these early products of the hydrolytic process are very rapidly changed. In the case of the liver enzyme, the results are similar, except that erythrodextrin is more constantly found; the liver enzyme differs from the others in the nature of the final product, which is dextrose, not maltose. By the prolonged action of all these enzymes, a form of achroodextrin (called by Seegen dystropo-dextrin) is produced which resists further conversion into sugar; this requires for its precipitation a larger percentage of alcohol than that required for the precipitation of the achroodextrin formed in an earlier stage of the hydrolysis.

W. D. H.

Chemistry of the Barley Plant with Reference to its Carbohydrate Constituents. By CHARLES F. CROSS and EDWARD J. BEVAN (*J. Fed. Inst. Brew.*, 1897, 3, 2—18).—In this paper, an account is given of the results which have been obtained by the authors in so far as they relate to the nature of the furfuraldehyde-yielding carbohydrates of the barley plant.

Seeing that the "spent grains" of the brewery contain considerable proportions of these carbohydrates, and that the latter, on acid hydrolysis, yield substances which are partially fermentable by yeast, it is suggested that these grains might be utilised by the brewer as an additional source of alcohol and extractive matter. Boiling for 2 hours in an open vessel with 1 per cent. sulphuric acid was found to be sufficient for their hydrolysis. A sample of malt-wort having a sp. gr. = 1.0944, to which the extract from the spent grains (furfuroids) had been added, fermented down to 1.018 after the addition of yeast.

A. C. C.

Tetrallylammonium Alum. By N. A. ORLOFF (*Chem. Centr.*, 1897, i, 1156; from *Pharm. Zeit. Russ.*, 36, 212—213. Compare *Abstr.*, 1896, i, 634, and 1897, i, 448).—Tetrallylammonium alum, $N(C_3H_5)_4Al(SO_4)_2 + 12H_2O$, crystallises in octahedra, and is very slightly soluble in water, whereas the anhydrous salt is easily soluble in water; the whole of the sulphuric anhydride cannot be expelled by heating in the Bunsen flame. Tetrallylammonium iodide, when dissolved in an equal weight of water, lowers the temperature 7°.

E. W. W.

Methylation of Hydrazine Hydrate. By CARL D. HARRIES and TAMEMASA HAGA (*Ber.*, 1898, 31, 56—64. Compare von Rothenburg, *Abstr.*, 1893, i, 410).—*Trimethylazonium iodide*, $NH_2 \cdot NMe_3I$, is obtained by agitating an aqueous solution of hydrazine hydrate with methylic iodide and caustic potash; it dissolves readily in water, and is somewhat soluble in boiling ethylic and amylic alcohols. It melts and decomposes at about 235°, and resembles ammonium chloride in crystalline structure. The *chloride* is hygroscopic, and the *hydroxide*

is an alkaline solid which absorbs carbonic anhydride and does not reduce Fehling's solution. When the hydroxide is submitted to distillation, it is resolved into methylic alcohol and unsymmetrical dimethylhydrazine, the *oxalate* of which crystallises in elongated plates and melts at 142—143°; dimethylamine is also produced. Agitation with methylic iodide and caustic potash converts trimethylazonium hydroxide into the iodide, and when the latter is heated with methylic iodide and methylic alcohol in a sealed tube at 125—130°, it yields tetramethylammonium iodide and a mixture of inflammable gases.

In the absence of caustic potash, the action of methylic iodide on hydrazine hydrate gives rise to a mixture of methylhydrazine and unsymmetrical dimethylhydrazine when excess of the base is employed; if methylic iodide is in excess, however, hydrazine hydriodide, trimethylazonium iodide, and methylhydrazine hydriodide are produced. Methylhydrazine *oxalate* crystallises from dilute alcohol in slender needles and melts at 166°.

Tribenzylidenemethylhydrazine, $(\text{CHPh}\cdot\text{N}\cdot\text{NMe})_2\text{CHPh}$, prepared from methylhydrazine (2 mols.) and benzaldehyde (3 mols.), crystallises from light petroleum in slender, white needles and melts at 109°. The substance does not reduce Fehling's solution, but is resolved into its components by hot dilute hydrochloric acid.

Benzylidenemethylhydrazine, $\text{CHPh}\cdot\text{N}\cdot\text{NHMe}$, is also obtained from methylhydrazine and benzaldehyde (1 mol.), and crystallises from alcohol in thick plates melting at 179°.

Symmetrical dimethylhydrazine (Harries and Klamt, Abstr., 1895, i, 262) can be prepared by acting on potassium diformylhydrazine with methylic iodide. The *oxalate* crystallises from absolute alcohol in flattened prisms, and melts at 132°; it reduces Fehling's solution when heated.

M. O. F.

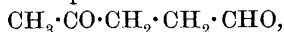
Hydrolysis of Sylvan to Levulinaldehyde (Constituents of Beech-wood Tar. I.). By CARL D. HARRIES (*Ber.*, 1898, 31, 37—47).—The sylvan (methylfurfuran) obtained by Atterberg (Abstr., 1880, 663) from the tar-oil of *Pinus sylvestris*, is also contained in beech-wood tar; it is shown to be 2-methylfurfuran,

$\text{O} \begin{cases} \text{CH}=\text{CH} \\ \text{CMe}:\text{CH} \end{cases}$, by its ready conversion into levulinaldehyde. When

150 kilos. of beech-wood tar are distilled, 10 kilos. of the distillate come over below 70°; this fraction is exhausted successively with 40 per cent. sodium hydrogen sulphite and 10 per cent. caustic soda solutions; the residual oil (about 5 kilos.) is fractionated with a long Le Bel column, and the fraction boiling at 60—70° (1.4 kilos.) is boiled with fresh quantities of sodium until no further action takes place; the residual liquid (1 kilo.) is again distilled, when the sylvan (β -methylfurfuran) comes over at 65° under 759 mm. pressure (850 grams); it has sp. gr. = 0.827 at 18°/18°.

When sylvan (500 grams) is boiled with methylic alcohol (1500 c.c.) and 80 per cent. methylic alcoholic hydrochloric acid (20 grams) for 24 hours, levulinmethylal is formed, together with a polymeride which boils at 180—220° under 10 mm. pressure, and is also formed when the methylal is allowed to remain with small quantities of acid.

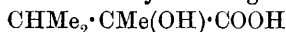
Levulinmethylal, $\text{CMeO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OMe})_2$, boils at $87-88^\circ$ under 17 mm. pressure, at $79-80^\circ$ under 13 mm.; its sp. gr. = 0.9684 at $18^\circ/18^\circ$; it yields an oily oxime, and an oily phenylhydrazone which slowly changes into phenylmethyldihydropyridazine (see below). *Levulinacetal*, $\text{CMeO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, is formed when ethyl alcoholic, instead of methyl alcoholic, hydrochloric acid is used; it boils at $92-93^\circ$ under 11–12 mm. pressure. *Levulinaldehyde*,



is formed when the methylal is boiled for a few minutes with 2 per cent. hydrochloric acid, the acid then neutralised with sodium hydrogen carbonate, and the aldehyde salted out with potassium carbonate, the precaution being taken to cover the aqueous solution with a layer of ether and shake after each addition of potassium carbonate. It boils at 70° under 12 mm. pressure, at 66° under 8.5 mm.; under atmospheric pressure, it boils at $186-188^\circ$ with slight decomposition; it has a sp. gr. = 1.0156 at 16° , and mixes with water in all proportions. Silver oxide oxidises it to levulinic acid; with ammonia, in ethereal solution, it forms a crystalline precipitate which is converted into 2-methylpyrroline by boiling with aqueous acetic acid; with phenylhydrazine acetate in aqueous solution, it yields *phenylmethyldihydropyridazine*, $\text{NPh} \langle \begin{smallmatrix} \text{N}=\text{CH} \\ \text{CMe}:\text{CH} \end{smallmatrix} \rangle \text{CH}_2$, which melts and decomposes at 197° ; it also forms a *dioxime* melting at $67-68^\circ$, a crystalline *semicarbazone*, and a crystalline compound with 2 mols. of sodium hydrogen sulphite.

C. F. B.

Constitution of Pinacolin. By CÆSAR POMERANZ (*Monatsh.*, 1897, 18, 575–581).—The results recently obtained by Delacre (Abstr., 1896, i, 591, and i, 662) are in favour of the symmetrical formula, $\text{O} \langle \begin{smallmatrix} \text{CMe}_2 \\ \text{CMe}_2 \end{smallmatrix} \rangle$, of Friedel and Silva for pinacolin. Accepting this, the trimethylpyruvic acid obtained by Glücksmann (Abstr., 1892, 38) on oxidising pinacolin, would have the formula $\text{O} \langle \begin{smallmatrix} \text{CMe}_2 \\ \text{CMe} \cdot \text{COOH} \end{smallmatrix} \rangle$, and to the hydroxy-acid obtained by reducing this, the formula



would be given, since, on being heated with sulphuric acid, it loses carbonic oxide and water, and yields methyl isopropyl ketone. The author has, however, prepared *hydroxymethylisopropylacetic acid* from methyl isopropyl ketone and hydrocyanic acid, by the method of Wislicenus and Urech; it crystallises from water, melts at 63° , is easily soluble in alcohol and ether, and is not identical with Glücksmann's hydroxy-acid. The symmetrical formula for pinacolin is therefore untenable.

The author confirms Butleroff's statement that the acid $\text{C}_5\text{H}_{10}\text{O}_3$, obtained on oxidising pinacolin, is identical with synthetical trimethylacetic acid; both acids melt at $34-35^\circ$, boil at 163° , and, in solutions of equal concentration, possess the same molecular conductivity. The calcium salts are also identical, crystallising with $4\text{H}_2\text{O}$, and not with $5\text{H}_2\text{O}$, as stated by Butleroff.

W. A. D.

Derivatives of Pinacolin. By E. CARLINFANTI (*Gazzetta*, 1897, 27, ii, 387—392).—In the hope of obtaining an acid of the constitution $\text{CMe}_3\cdot\text{CHMe}\cdot\text{COOH}$, the author has prepared *pinacolin cyanhydrin*, $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{CN}$, by treating a mixture of pinacolin and potassium cyanide with hydrochloric acid at 0° ; on fractionally distilling the product, a small yield of the cyanhydrin was obtained as an unstable, white, crystalline substance melting at $82\text{--}87^\circ$ which has the normal molecular weight in freezing benzene. On hydrolysis with dilute potash, sulphuric acid, hydrochloric acid, or hydrogen peroxide, it yields pinacolin instead of the carboxylic acid.

Pinacolinsemicurbazone, $\text{C}_7\text{H}_{15}\text{N}_3\text{O}$, which is readily prepared, crystallises in lustrous, white needles melting at 175° . Pinacolin reacts with phenylhydrazine and parabromophenylhydrazine, yielding resinous products. W. J. P.

Determination of Acetyl Groups in Organic Compounds. By FRANZ WENZEL (*Monatsh.*, 1897, 18, 659—672).—The author points out the limitations of methods at present in use, and describes a process which is universally applicable. It consists in hydrolysing the acetyl compound with dilute sulphuric acid (2 acid:1 water), and distilling the acetic acid formed into decinormal potash. The distillate should be free from sulphurous acid when titrated against decinormal iodine; if this is not the case, the sulphuric acid used for hydrolysis must be diluted. In the case of sulphur compounds, in order to prevent error by the liberation of hydrogen sulphide, cadmium sulphate is mixed with the substance before hydrolysis; if the compound contains a halogen, silver sulphate must be added.

To carry out the process, 0.2—0.4 gram of the compound is placed in a distilling flask connected with a short reflux condenser, the further end of which is bent so as to pass down into a second smaller distilling flask. The side tube of this flask is connected to the upper end of a vertical condenser; this dips into decinormal potash contained in a pump-flask, in which a vacuum can be produced. Three c.c. of the dilute sulphuric acid is added to the acetyl compound, and, after some time, 3 c.c. of water; the mixture is then heated at $60\text{--}70^\circ$ until complete hydrolysis is effected. Twenty c.c. of a solution containing 100 grams of metaphosphoric acid and 450 grams of crystallised disodium phosphate in a litre of water are then added, the flask is connected with a hydrogen generating apparatus, and the liquid distilled to dryness under greatly reduced pressure. Twenty c.c. of water is added and the distillation repeated. The second distilling flask serves to prevent traces of phosphoric acid being carried over into the decinormal alkali; during the distillation, it is heated in water to the same temperature as the flask containing the hydrolysed compound. After the second distillation, the apparatus is filled with hydrogen, the pump-flask and its condenser disconnected, and the excess of alkali determined by titration. The author has verified the accuracy of his method by the analysis of 41 acetyl compounds of widely differing constitution. W. A. D.

V. Meyer's Etherification Law. By ANGELO ANGELI (*Real. Accad. Linc.*, 1896, [v], 5, i, 84—88).—V. Meyer considers that, in

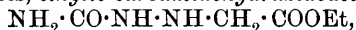
the action of an alcohol, $R'\cdot OH$, on an acid, $CR_2\cdot COOH$, in presence of hydrogen chloride, water is directly eliminated from the alcohol and acid with formation of the salt $CR_2\cdot COOR'$. The author considers the change to be of a more complex character and to involve the intermediate formation of compounds of the constitution $CR_2\cdot C(OH)_2\cdot OR'$ or $CR_2\cdot C(OH)(OR')Cl$. Evidence is quoted in favour of this view, which is also applied to other reactions, such as those involved in the formation of nitriles and oximes.

W. J. P.

Hydrazidoacetic Acid. By WILHELM TRAUBE and E. HOFFA (*Ber.*, 1898, 31, 162—169. Compare Abstr., 1897, i, 138).—Pure hydrazidoacetic acid is best obtained by the following method. *o*-Hydroxybenzylidenehydrazidoacetic acid is suspended in water, treated with sulphuric acid (1 mol.), and subjected to steam distillation until no more salicylaldehyde passes over; the sulphuric acid is precipitated with baryta water, the excess of the latter removed by warming with ammonium carbonate, the filtrate evaporated under diminished pressure, and the syrupy residue rubbed with alcohol; the crystalline mass is then dissolved in water and dropped into absolute alcohol. After this operation has been repeated several times, the purified acid is obtained in the form of needles melting at 152° . It dissolves readily in water, but is insoluble in alcohol, ether, or benzene, readily reduces Fehling's solution, and gives salts with mineral acids but not with bases. The *hydrochloride* of the ethylic salt, $NH_2\cdot NH\cdot CH_2\cdot COOEt, HCl$, obtained in the usual manner, crystallises from alcohol in glistening plates melting at 153° , and is readily soluble in water. The ethylic salt itself was only obtained as an oil.

Ethylic dibenzoylhydrazidoacetate, $NBz_2\cdot NH\cdot CH_2\cdot COOEt$, which crystallises from alcohol in needles melting at 113° , is readily soluble in alcohol, ether, or benzene, and does not reduce Fehling's solution. When hydrolysed by alkalis, it gives metallic salts of the dibenzoylated acid.

The three products, *ethylic carbamidohydrazidoacetate*,



ethylic amidohydantoate, $NH_2\cdot CO\cdot N(NH_2)\cdot CH_2\cdot COOEt$, and *amido-*

hydantoin, $\begin{array}{c} CH_2\cdot N(NH_2) \\ | \\ CO\text{---}NH \end{array} > CO$, are obtained when the hydrochloride of

ethylic hydrazidoacetate is treated with an excess of potassium cyanate in aqueous solution; after remaining for some time, the solution is evaporated to dryness under diminished pressure, and the residue extracted with hot alcohol until the extract no longer reduces Fehling's solution. The solid residue obtained when the alcoholic solution is evaporated under reduced pressure is extracted with large quantities of hot benzene, and on cooling ethylic carbamidohydrazidoacetate is deposited in the form of slender needles melting at 122° . The benzene mother liquor from these crystals yields ethylic amidohydantoate, which crystallises in colourless prisms melting at $70\text{--}74^\circ$. It is readily soluble in water, like its isomeride, but only reduces Fehling's solution after boiling for some time. It yields a *benzylidene* derivative which crystallises in needles melting at 150° .

The portion of the solid residue which is insoluble in benzene is dissolved in water, and the solution, when acidified and treated with

benzaldehyde, yields *benzylideneamidohydantoin* melting at 244°. A better yield of this compound is obtained when the solid residue produced in the reaction of ethylic hydrazidoacetate with an excess of potassium cyanate is hydrolysed with dilute sulphuric acid and the solution then shaken with benzaldehyde; the benzylidene derivative is somewhat difficult to hydrolyse. *Amidohydantoin hydrochloride* melts at 203°, is readily soluble in water, sparingly in alcohol.

When a solution of phenyl thiocarbamate (1 mol.) in alcohol is added to an aqueous solution of hydrazidoacetic acid (1 mol.) and potassium hydroxide (1 mol.), and the mixture warmed for a few minutes on the water bath, and, after cooling, mixed with absolute alcohol, *potassium phenylthioamidohydantoate* separates in crystals; it melts at 190°, is very readily soluble in water, and on the addition of hydrochloric acid yields *phenylthioamidohydantoic acid*,



which crystallises in needles, is moderately soluble in water, and melts at 135°. The acid yields a *benzylidene* derivative melting at 245°, and when heated with water at 103° loses carbonic anhydride, yielding *phenylthioamidohydantoin*, which melts at 165°. *Methylthioamidohydantoin* melts at 120°.

J. J. S.

Action of Chlorine on Isovaleric Acid. By CLEMENTE MONTE-MARTINI. (*Gazzetta*, 1897, 27, ii, 368—374).—On passing chlorine into isovaleric acid at 90°, absorption occurs rapidly in sunlight, but very slowly in its absence; when the weight of the flask indicates that sufficient chlorine has been absorbed to form a monochloro-derivative, the product is converted into an ethylic salt and *ethylic β-chlorisovalerate* may then be isolated by fractional distillation. It boils at 101—103° under 30 mm. pressure, and at ordinary pressures, with slight decomposition at 184—190°; it is heavier than, and insoluble in, water. The monochloro-derivative is accompanied by smaller quantities of a dichloro-derivative. Ethylic β-chlorisovalerate does not react with potassium cyanide, silver cyanide, or ethylamine, but converts silver hydroxide partly into chloride and partly into metal; it condenses with ethylic malonate, but no definite compound could be isolated from the product. The ethylic salt does not react satisfactorily with phenylhydrazine, but on heating the crude acid obtained by chlorination, with phenylhydrazine, a violent action occurs and on treatment with water and ether a *phenyldimethylpyrazolidone*, $\text{CMe}_2 \cdot \text{NPh} \gg \text{NH}$, is obtained; it crystallises in lustrous needles melting at 109—110°, and is not decomposed by hydrochloric acid or potash. Since the phenyldimethylpyrazolidone of the constitution $\text{CMe}_2 \cdot \text{NH} \gg \text{NPh}$, prepared by Prentice, differs from the author's compound, the latter must have the composition assigned above; it follows that the chlorisovaleric acid now described contains the chlorine in the β-position.

W. J. P.

Derivatives of Behenic Acid. By GIULIO FILETI (*Gazzetta*, 1897, 27, ii, 298—302).—The author has prepared behenic acid by

M. Fileti and Ponzio's method (*Gazzetta*, 1893, 23, ii, 392) of treating erucic acid with moist phosphorus tri-iodide. When treated with bromine and red phosphorus by Volhard's method, it yields *α*-bromobehenic acid, $C_{22}H_{43}BrO_2$, which melts at 70° , and is soluble in the ordinary organic solvents; its *ethylic* salt, $C_{24}H_{47}BrO_2$, is crystalline and melts at $49-51^\circ$.

α-Hydroxybehenic acid, $C_{22}H_{44}O_3$, is obtained by heating *α*-bromobehenic acid with concentrated aqueous potash at 130° in a reflux apparatus, pouring into water, and precipitating with sulphuric acid; it melts at $96-97^\circ$, is very soluble in the ordinary organic solvents, and yields an *ethylic* salt melting at $70-71^\circ$. If alcoholic potash is used in preparing the hydroxy-acid, a small yield is obtained, most of the product being converted into *α*-ethoxybehenic acid which melts at 60° .

α-Cyanobehenic acid, $C_{23}H_{43}O_2N$, is prepared by heating the bromo-acid in alcoholic solution with potassium cyanide and decomposing the product with hydrochloric acid; it crystallises in white needles, melts at $87-89^\circ$ and decomposes at 180° , probably yielding the nitrite. When boiled with alcoholic soda, it yields *eicosymalonic acid*, $C_{23}H_{43}O_4$, which crystallises in needles, melts at $119-120^\circ$, and gives off carbonic anhydride at 150° , probably yielding behenic acid.

W. J. P.

Active Constituent of Castor Oil. By HANS MEYER (*Chem. Centr.*, 1897, i, 662; from *Arch. expt. Path. Pharm.*, 38, 336-345. Compare Abstr., 1897, i, 591-592).—The purgative action of castor oil is not affected by heating the oil to 300° , or by the action of dry hydrogen chloride. Ricinoleic acid, which is, as Buchheim observed, just as effective as castor oil, does not lose this property by heating to 300° , or by boiling with potassium hydroxide solution, but it is converted by the action of mineral acids into *ψ*-ricinoleic acid, whose alkylic salts are inactive. Ricinolamide is inactive, but yields an active ricinoleic acid. Castor oil owes its purgative property to the presence of ricinoleic acid, or such compounds of it as are decomposed into ricinoleic acid in the intestines: thus magnesium ricinoleate which is not decomposed is inactive. Barium ricinoleate, when purified by repeated crystallisation from alcohol, melts at 132° , and contains water which is not expelled at 120° ; the cadmium salt is anhydrous. *Ethylic ricinoleate*, prepared by heating sodium ricinoleate with ethylic iodide at $150-170^\circ$, is a light brown liquid of sp. gr. = 0.9176 at $20^\circ/24^\circ$; *methylic ricinoleate* is prepared in a similar way. *Ethylic ψ-ricinoleate*, which has a sp. gr. = 0.9294 at $20^\circ/24^\circ$, is prepared by passing hydrogen chloride into a hot solution of ricinoleic acid in absolute alcohol, treating the product with water and calcium carbonate, and extracting with light petroleum. Barium *ψ*-ricinoleate melts at $117-118^\circ$.

E. W. W.

Separation of the Two Desmotropic Forms of Ethylic Acetoacetate. By ROBERT SCHIFF (*Ber.*, 1898, 31, 205-209).—By the action of benzylideneaniline on ethylic acetoacetate under different conditions, three distinct isomeric additive products have been prepared. When molecular quantities of the two substances are rubbed

together in a dish which is well cooled with water, a thick syrup is obtained, but this soon sets into a hard, white, crystalline mass. After dissolving in benzene and precipitating with light petroleum, small, crystalline aggregates of the compound $C_{19}H_{21}NO_3$ are obtained; its melting point is $93-95^\circ$. When the two substances react in the proportion of 1 molecule of benzylidene aniline to 2 of the acetate, the product, after freeing from the excess of acetate and purification as above, melts at 103° . If, however, a few drops (0.2 gram) of piperidine are introduced in the second reaction, a third isomeride, melting at 78° , is obtained. All three substances are optically inactive, and have the same molecular weight.

The author considers that his results support the view that ethylic acetoacetate is a mixture of the "keto" and "enol" forms. The substance melting at 78° is supposed to be the derivative of the "keto" form, and the one melting at 103° is a derivative of the "enol" form. The product, which melts at 95° , is a mixture of the other two, and can readily be obtained synthetically by crystallising a mixture of the two isomerides melting at 78° and 103° . Both the latter compounds can be converted into the mixture melting at 95° by warming with dilute methylic or ethylic alcohol, or by heating for some time at a temperature slightly above their melting points. The two compounds melting at 95° and 103° readily yield deep cherry-red colorations with 35—40 per cent. alcohol and ferric chloride; the compound melting at 78° gives a yellow coloration, which changes to red in the course of a few hours, owing probably to gradual enolisation. Concentrated alcohol causes this change much more rapidly. The enol form (103°) appears to dissolve to a certain extent in alkalis and alkali carbonates.

J. J. S.

Formation of Ethereal Salts. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, 18, 629—657. Compare *Abstr.*, 1895, i, 420; 1896, i, 95; 1897, i, 55; and this vol., i, 30).—The author discusses the results he has hitherto obtained; his views are summarised as follows. (1) When alkylic iodides interact with the acid salts of unsymmetrical dicarboxylic acids, the alkyl radicle becomes attached to the carboxyl group which has the greater electrolytic dissociation constant. (2) A similar law regulates the interaction of alcohols with the anhydrides of unsymmetrical dicarboxylic acids. (3) The formation of ethereal salts by the action of these acids on alcohols in the presence of hydrogen chloride is independent of dissociation constants, and depends solely on the structure of the acid molecule, as pointed out by Victor Meyer. The same law holds for the alkaline hydrolysis of the salts. (4) This similarity between the behaviour of acids with alcohols in presence of hydrogen chloride, and that of the ethereal salts on hydrolysis with alkalis, is best explained by assuming that, in both cases, an intermediate compound is formed by addition to the carboxyl group, as was originally assumed by Henry.

The author divides the methods of formation of ethereal salts into two classes; the first, in which the governing factor is the strength of the carboxyl group, includes the methods based on the interaction of salts of the acid with alkylic iodides, and of alcohols with acid

anhydrides. The interaction of alcohols and acids in presence of hydrogen chloride is a method of the second class, in which the conditioning factor is molecular constitution. A series of experiments are described, showing that the interaction of acid and alcohol in presence of sulphuric acid is also a method of the second class.

In the presence of a small quantity of sulphuric acid, β -monomethylic hemipinate is almost the sole product of the action of methylic alcohol on hemipinic acid; when an excess of sulphuric acid is used, and the mixture cooled, hemipinic anhydride alone is formed, but on heating the mixture, dimethylic hemipinate and traces of the α - and β -monomethylic salts are obtained. Methylic alcohol does not combine with hemipinic acid in presence of methylic potassium sulphate; α -monomethylic hemipinate is formed, however, when the acid and alcohol are heated alone in a sealed tube at 100° ; this is probably due to the intermediate formation of hemipinic anhydride (compare this vol., i, 30). Symmetrical tribromobenzoic acid is not acted on when heated with methylic alcohol at 100° , or when the mixture is boiled with a small quantity of sulphuric acid; if, however, an excess of this acid is used, a 12 per cent. yield of the methylic salt is obtained.

W. A. D.

Preparation of Pure Oxalic Acid. By RUDOLF RIECHELMANN (*Chem. Centr.*, 1897, i, 539; from *Zeit. f. öffentl. Chem.*, 3, 13).—Pure oxalic acid is obtained from the commercial acid by crystallising once from ether, and then once from water. Comparatively large quantities of the acid may be conveniently dissolved in ether by using a Soxhlet's extractor fitted with a Schleicher and Schüll's cartridge.

E. W. W.

Zirconium Oxalates. By FRANCIS P. VENABLE and CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1897, 19, 12—18).—On adding a saturated solution of oxalic acid to a slightly acid solution of zirconium chloride, a gelatinous precipitate, of the composition $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 2\text{Zr}(\text{OH})_4$ is produced, and the filtrate after a time yields another precipitate, $2\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 3\text{Zr}(\text{OH})_4$; these basic oxalates are soluble in acids with difficulty, and are in an extremely fine state of division, passing through the best filter paper. As all the oxalates and double oxalates examined lose oxalic acid when heated at 100° , they had to be dried between filter paper.

When zirconium hydroxide dissolved in excess of a solution of oxalic acid is evaporated, a *salt* of the composition $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{C}_2\text{O}_4 + 8\text{H}_2\text{O}$ is produced, and not the normal oxalate. Zirconium oxalate shows no decided tendency to form definite combinations with the alkali oxalates, but rather a power to crystallise with them in any proportions.

When a solution of zirconium hydroxide in oxalic acid is nearly neutralised with sodium hydroxide and evaporated, small, hard, prismatic crystals are obtained, probably of the composition $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 3\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 + 5\text{H}_2\text{O}$. Under similar conditions, potassium and ammonium hydroxides yield respectively the *salts* $2\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 2\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 + 8\text{H}_2\text{O}$ and $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 2(\text{NH}_4)_2\text{C}_2\text{O}_4$; the latter could not be recrystallised without change.

A. W. C.

Action of Dimethylamine on Diethylic Fumarate and Maleate. By WILHELM KÖRNER and ANGELO MENOZZI (*Real. Accad. Linc.*, 1896, [v], 5, i, 456—459).—On heating diethylic fumarate with an alcoholic solution of dimethylamine for 3 days in a closed tube at 105—110°, distilling the product from a water bath, and adding ether to the residue, tetramethylasparagine is deposited whilst diethylic dimethylaspartate remains dissolved in the ether.

Tetramethylasparagine, $\text{NMe}_2 \cdot \text{CH}(\text{NMe}_2) \cdot \text{CH}_2 \cdot \text{COOH}$, crystallises in colourless needles melting at about 104°, and is very soluble in alcohol; when heated with barium hydroxide, it yields dimethylamine and dimethylaspartic acid, together with fumaric acid resulting from the decomposition of the latter.

Diethylic dimethylaspartate, $\text{C}_{10}\text{H}_{19}\text{NO}_4$, is a highly refractive liquid which has a slight odour and is very sparingly soluble in water; it has the sp. gravities = 1.0418, 1.0306, and 0.9702 at 0°, 15°, and 50° respectively, referred to water at 0°. When heated with barium hydroxide solution in a closed tube, it yields *barium dimethylaspartate* crystallising in needles; the acid itself, $\text{C}_6\text{H}_{11}\text{NO}_4$, crystallises in large, colourless, monosymmetric prisms melting at 185°; $\alpha : b : c = 1.2141 : 1 : 0.6340$; $\beta = 78^\circ 19'$. The diethylic salt gives a quantitative yield of diethylic fumarate when boiled with sulphuric acid.

On heating diethylic maleate with dimethylamine solution, the same products are obtained as with the fumarate. W. J. P.

Homologues of Ethylic Oxalacetate. By WILHELM WISLICENUS and MAX KIESEWETTER (*Ber.*, 1898, 31, 194—200).—Ethylic oxalobutyrate, like the corresponding oxalopropionate, readily decomposes when heated, ethylic ethylmalonate being formed and carbonic oxide evolved; the homologues, however, behave towards ammonia in a different manner from ethylic oxalate itself, as an amidoimide is formed, and not an additive compound. This amido-imide is analogous in constitution to the substance obtained by the action of aniline on ethylic oxalopropionate (Wislicenus and Spiro, *Abstr.*, 1890, 378).

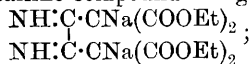
Amidocitraconimide, $\text{NH} \begin{array}{c} \diagup \text{CO} \cdot \text{C} \cdot \text{NH}_2 \\ | \\ \text{CO} \cdot \text{CMe} \end{array}$, obtained by the action of ammonia on ethylic oxalopropionate, forms yellow crystals, melts at 230°, and is decomposed by boiling aqueous soda, with evolution of ammonia and formation of sodium oxalate; ethylic oxalobutyrate yields a similar compound, which also forms yellow crystals, melts at 204°, and is probably *amidoethylmaleinimide*, $\text{NH} \begin{array}{c} \diagup \text{CO} \cdot \text{C} \cdot \text{NH}_2 \\ | \\ \text{CO} \cdot \text{CEt} \end{array}$.

Ethylic oxalopropionate reacts with benzaldehyde in a similar manner to ethylic oxalacetate, *ethylic ketophenylhomoparaconate*, $\text{O} \begin{array}{c} \diagup \text{CO} - \text{CO} \\ | \\ \text{CHPh} \cdot \text{CMe} \cdot \text{COOEt} \end{array}$, being formed; this, which is an oil, has not yet been obtained pure. It is decomposed by boiling dilute sulphuric acid, yielding benzaldehyde, carbonic anhydride, alcohol, and propionylformic acid, its constitution being thus proved.

Ethylic oxalisobutyrate (ethylic dimethyloxalacetate),
 $\text{COOEt} \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{COOEt}$,

is formed in very small amount when ethylic sodio-oxalopropionate is treated with methylic iodide, but has only been obtained as a slightly impure oil boiling between 225 and 230° without any evolution of carbonic oxide. When heated with alcoholic soda, it yields oxalic and isobutyric acids, so that no doubt exists as to its constitution. Ammonia decomposes it with formation of oxamide and isobutyramide, whilst aniline yields oxanilide, and with phenylhydrazine it forms a *hydrazone*, $\text{COOEt} \cdot \text{C}(\text{N}_2\text{HPh}) \cdot \text{CMe}_2 \cdot \text{COOEt}$, which melts at 90—91° and cannot be made to yield a pyrazolone. A. H.

Action of Cyanogen on Ethylic Sodiomalonnate. By WILHELM TRAUBE (*Ber.*, 1898, 31, 191—193).—Ethylic sodiomalonnate absorbs cyanogen with development of heat, a red, crystalline compound being formed which most probably has the constitution



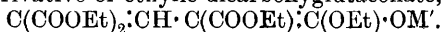
water converts this into a substance of the formula $\text{C}_{12}\text{H}_{14}\text{O}_8\text{N}_2\text{Na}_2$, which crystallises in brownish needles, is sparingly soluble in water, and on treatment with hydrochloric acid yields a yellowish substance, $\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_2$, which may also be obtained by the direct action of hydrochloric acid on the red compound. The free acid, corresponding with the red salt, is formed when the latter is warmed with aqueous soda and then acidified; it crystallises in pale yellow needles, is decomposed by boiling water, and with phenylhydrazine acetate yields a brown, crystalline *derivative* melting at 210°.

When the red sodium salt is treated with methylic iodide, a derivative, $\text{C}_{14}\text{H}_{16}\text{O}_6\text{N}_2$, is formed which crystallises in deep yellow needles and melts at 150°. Similar compounds are formed by the action of cyanogen on ethylic sodioacetoacetate and other analogous compounds. A. H.

Copper Derivatives of Ethylic Dicarboxyglutaconate. By WILHELM WISLICENUS (*Ber.*, 1898, 31, 140—142).—Ethylic dicarboxyglutaconate yields two copper derivatives, *normal*, $(\text{C}_{15}\text{H}_{21}\text{O}_8)_2\text{Cu}$, and *basic*, $\text{C}_{15}\text{H}_{21}\text{O}_8 \cdot \text{Cu} \cdot \text{OH}$. The normal compound is readily obtained when a 15 per cent. alcoholic solution of the ethylic salt is treated with the requisite quantity of copper acetate dissolved in 15—20 times its weight of water. It crystallises from alcohol in small, yellowish-green needles melting at 175—176°, and its alcoholic solution gives a deep violet coloration with ferric chloride.

The basic derivative is obtained together with the normal one when warm alcoholic solutions of the ethylic salt and copper acetate are used, or, still better, when an aqueous solution of the sodium derivative of the ethylic salt is precipitated with an excess of copper acetate solution. It can be separated from the normal derivative by the aid of methylic alcohol, in which it is only sparingly soluble. Recrystallised from a large quantity of hot methylic alcohol, it is obtained in bluish-green prisms melting at 193—195°. It also gives a violet coloration with ferric chloride.

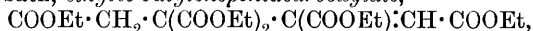
As it is probable that in all stable metallic derivatives the metal is directly combined with oxygen, the following constitution is given to the metallic derivative of ethylic dicarboxyglutaconate,



It is thought probable that the ethylic salt, like ethylic acetoacetate, consists of a mixture of a small quantity of the "enol" and much of the "keto" forms, and that by the action of alkalis, ferric chloride, copper acetate, &c., it is rapidly converted into metallic derivatives of the "enol" type.

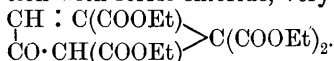
J. J. S.

Syntheses with Ethylic Chlorofumarate. By WALTER BECKH (*Ber.*, 1898, 31, 47—51).—When ethylic ethane-*aaa*₁-tricarboxylate is mixed with sodium ethoxide in cooled alcoholic solution, ethylic chlorofumarate added, and the mixture finally warmed for an hour on the water bath, *ethylic butylenepentacarboxylate*,

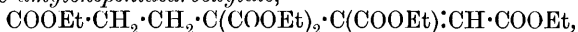


is formed, and separates as an oil when the alcohol is distilled off and the residue poured into water. It boils at 229—231° under 13 mm. pressure; it is hydrolysed by boiling with baryta water, and the free *acid*, which is very soluble in water, can be obtained crystalline and melts at 173—176°.

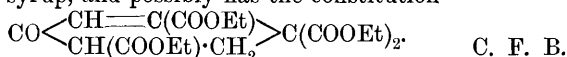
A second product is formed in addition, but this is more conveniently obtained by mixing ethylic butylenepentacarboxylate (1 mol.) with sodium (1 atom) and a few drops of absolute alcohol, and heating at 120°. The product, when dissolved in water and acidified, yields an oil which does not boil without some decomposition, even under diminished pressure; it has marked acid properties, and gives a claret coloration with ferric chloride, very possibly it is a ketopentene derivative,



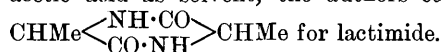
Ethylic amylenepentacarboxylate,



was prepared from ethylic carboxyglutarate (propane-*aaa*₁-tricarboxylate) (Emery, *Abstr.*, 1891, 547; in its formation, for ethylic β -bromopropionate the analogous iodo-compound is substituted with advantage) and ethylic chlorofumarate; it boils at 240—250° under 15 mm. pressure. It also condenses with sodium ethoxide at 120°; the product is a syrup, and possibly has the constitution



Molecular Weight of Lactimide. By GEORGE M. RICHARDSON and MAXWELL ADAMS (*Amer. Chem. J.*, 1898, 20, 129—133).—By determining its molecular weight by the cryoscopic method, using acetic acid as solvent, the authors confirm the structural formula,



W. A. D.

Stability of Imides of Dibasic Acids. By ARTURO MIOLATI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 375—380).—In continuation of his previous work (*Abstr.*, 1896, ii, 242), the author has made further determinations of the velocity of hydrolysis of the imides of dibasic acids; the velocity constants *Ac* are given in the accompanying table.

No determinations were possible with orthobenzoicisulphide, the

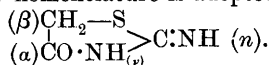
Substance.	<i>Ac</i>	Substance.	<i>Ac</i>
Citraconic imide	1·2139	Quinolinic imide	0·2561
Pyrocinchonic imide	0·3184	Cinchomeric imide	0·3977
Phthalimide	0·08705		

aqueous solution being acid, and immediately becoming neutral on adding 1 molecular proportion of soda. W. J. P.

Biuret Reactions. By HUGO SCHIFF (*Annalen*, 1897, 299, 236—266. Compare Abstr., 1896, i, 284 and 635).—The author describes in detail the results already published. The derivatives of biuret, malonamide, and oxamide which give the biuret reaction are distinguished from those which do not. M. O. F.

Thiocarbamide Derivatives. By RUDOLF ANDREASCH (*Ber.*, 1898, 31, 137—138).—Thiohydantoin was obtained by treating the different thiocarbamides with ethylic chloracetate or α -bromopropionate in alcoholic solution, and after precipitation with ammonia were extracted with ether.

Hantzsch's system of nomenclature is adopted.



n-Ethylthiohydantoin, $\text{C}_5\text{H}_8\text{N}_2\text{SO}$, forms colourless needles melting at 144° . *n-v*-Diethylthiohydantoin forms colourless needles, is very readily soluble, and melts at 41° ; β -Methyl-*n*-ethylthiohydantoin, ethylallylthiohydantoin, and ethylphenylthiohydantoin were obtained in the form of yellowish, syrupy oils.

Phenyl- β -benzylidenethylthiohydantoin, $\text{C}_{18}\text{H}_{16}\text{N}_2\text{SO}$, obtained by the action of benzaldehyde on ethylphenylthiohydantoin, melts at 90° . Phenyl- β -methylthiohydantoin melts at 101° .

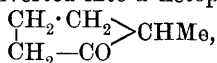
Thioparabanic acids were obtained by passing cyanogen gas into the alcoholic solutions of the thiocarbamides and then heating the resulting cyanides with hydrochloric acid; they were mostly purified by extraction with ether, and when heated with silver nitrate in alcoholic solution gave the corresponding parabanic acids.

Ethylthioparabanic acid forms golden-yellow needles melting at 66° . Ethylparabanic acid crystallises in colourless needles melting at 45° . Diethylthioparabanic acid forms flat, yellow needles or thick prisms melting at 102° . Diethylparabanic acid, colourless needles melting at 46° . Methylthioethylthioparabanic acid, slender, yellow needles melting at 62° . Methylallylthioparabanic acid melts at 56° and methylallylparabanic acid at $42-43^\circ$. Ethylallylthioparabanic acid melts at 54° , and ethylallylparabanic acid at 66° . Phenylmethylthioparabanic acid, which melts at 170° and crystallises in sulphur-yellow needles or orange-yellow, six-sided plates, is decomposed by barium carbonate, yielding oxalic acid and phenylmethylthiocarbamide. Phenylmethylparabanic acid melts at 148° , phenylethylthioparabanic acid, which, in appearance, resembles lead iodide, melts at 174° and phenylethylparabanic acid at 97° . Diphenyl-

thioparabanic acid crystallises in bronze-coloured, woolly needles melting at 228°. *Diparatolylthioparabanic acid* melts at 236°.

Unsymmetrical disubstituted thiocarbamides do not combine with cyanogen. J. J. S.

α -Methyladipic Anhydride and 2-Methylketopentamethylene. By CLEMENTE MONTEMARTINI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 228—231. Compare Abstr., 1897, i, 19).—On distilling α -methyladipic acid with acetic chloride under reduced pressure, it is converted into a very unstable anhydride, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO} \\ | \quad \quad \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \end{array} \text{O}$, which, by distillation, is partially converted into a ketopentamethylene,

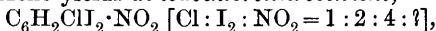


with loss of carbonic anhydride.

2-Methylketopentamethylene, which is best prepared by distilling α -methyladipic acid with lime and iron filings, boils at 142—144°, has a mint-like odour and is lighter than water. Its semicarbazone, $\text{C}_7\text{H}_{13}\text{N}_3\text{O}$, forms minute crystals melting at 171°. W. J. P.

Iodine Derivatives of Monochlorobenzene. By CONSTANTIN I. ISTRATI (*Chem. Centr.*, 1897, i, 1161; from *Bull. Soc. Sciënte*, 6, 47—55).—When a mixture of 250 grams of monochlorobenzene with 500 grams of iodine and 350 c.c. of sulphuric acid is boiled for 38 hours, the product consists of two distinct layers of liquid. By shaking the whole with water, it forms a rather viscous liquid which deposits a coarsely crystalline mass and a brownish-red precipitate of francin. The decanted liquid is neutralised with calcium and barium carbonates, the excess of iodine and the francin are removed by concentrated potassium hydroxide solution, and the residual liquid then thoroughly washed with boiling water; when this liquid is distilled under 60 mm. pressure, a liquid and a solid substance come over at 200—280°. The latter is also left behind when the distillation is continued under atmospheric pressure from 135—310°, or by distilling to 270° in a vacuum. By repeatedly crystallising from chloroform, it yields *chlorotri-iodobenzene*, $\text{C}_6\text{H}_2\text{ClI}_3$ [$\text{Cl}:\text{I}_3=1:2:4:6$], melting at 162—164°.

The liquid portion of the distillate, when fractionated, yields chlorobenzene, large, colourless, transparent crystals of iodobenzene, and finally *chlorodi-iodobenzene*, $\text{C}_6\text{H}_3\text{ClI}_2$ [$\text{Cl}:\text{I}_2=1:2:4$], a colourless liquid which gradually becomes faintly red, boils at 221° under 78 mm. pressure, remains liquid at -12° , is soluble in alcohol and chloroform, and has a remarkably high sp. gr. = 2.5547—2.5552 at 0° , and 2.5197—2.5201 at 25° . When treated with fuming nitric acid at 80° , di-iodochlorobenzene yields *di-iodochloronitrobenzene*,



an extremely volatile substance which crystallises from alcohol and melts at 94—95°. E. W. W.

The Explosive Decomposition of Nitro-compounds when Mixed with Substances Rich in Oxygen. By CHRISTIAN GÖTTIG (*Ber.*, 1898, 31, 25—28).—The powder examined contained in 100 parts:

barium nitrate, 9.83; nitrotoluenes (mixture of 2:4:6-trinitrotoluene with 2-nitrotoluene), 22.22; nitrocelluloses, 67.96; the percentage of nitrogen, estimated by the Dumas method, was 12.33. Some of the powder was exploded in a small chamber by means of a platinum wire heated electrically. The solid residue formed 14.28 per cent. of the whole, and contained, in 100 parts, organic matter (carbon), 9.51; barium carbonate, 64.44; residue insoluble in acids, with some alkali carbonates, iron compounds, &c., 26.05. The water formed amounted to 8.64 per cent. of the powder. The (dry) gases formed in the explosion contained, in 100 vols.: nitric oxide, 10.75; carbonic anhydride, 27.48; carbonic oxide, 36.02; methane, 9.01; hydrogen, 1.94; nitrogen, 14.80. The following equation is given as representing the decomposition, $11\text{C}_{12}\text{H}_{14}(\text{NO}_{3/6}\text{O}_4 + 10\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3 + 4\text{Ba}(\text{NO}_3)_2 = 4\text{BaCO}_3 + 49\text{H}_2\text{O} + 9\text{C} + 93\text{CO} + 72\text{CO}_2 + 28\text{NO} + 5\text{H}_2 + 24\text{CH}_4 + 38\text{N}_2$.

C. F. B.

Composition of Wool Fat. V. By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1898, 31, 97—103. Compare Abstr., 1896, i, 522; 1897, i, 180).—The soft fat, left after the removal of the wool wax, as already described, amounts to about 85—90 per cent. of the whole, and yields on hydrolysis about 40—45 per cent. of acids; these, which consist chiefly of an oily acid of unknown constitution, myristic acid, and carnaubaic acid, will be more particularly described in a further communication.

The alcohols obtained from the soft fat do not appear to contain any cholesterol, but can be divided into nearly equal fractions, one of which is insoluble in cold methylic alcohol, whilst the other is readily soluble. The former of these agrees in most of its properties with Schulze's ischolesterol (this *Journal*, 1873, 920), but appears to differ from it in crystalline form, solubility, and composition. It is insoluble in water and methylic alcohol, but readily soluble in most other solvents, and crystallises in short, thick, microscopic prisms, which melt at 137—138° when dry. The air-dried substance loses 2.7 per cent. of water at 80°, leaving a residue which has the composition $(\text{C}_{26}\text{H}_{45}\text{O})_2\text{O}$. When a drop of sulphuric acid is added to its solution in acetic acid, a yellow solution with a green fluorescence is produced, showing a characteristic absorption band between the lines D and E of the solar spectrum.

The second fraction consists of a thick, honey-like mass, which will be described in a further communication.

The examination of the alcohols obtained from the wool wax has shown that a small amount of cerylic alcohol is present. Among the acids obtained from the same substance, a small amount of a compound has been isolated, which agrees in nearly all its properties with cerotic acid, but appears to differ from the latter in its behaviour towards solvents and in the fact that its magnesium salt melts at 174—176°, whereas magnesium cerotate is stated to have the melting point 140—145°.

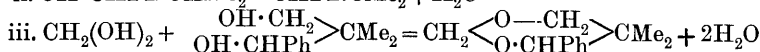
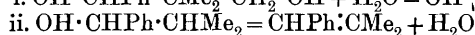
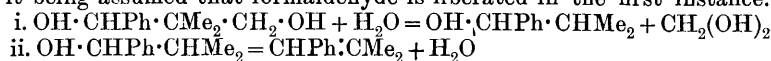
A. H.

The Glycol obtained from Isobutaldehyde and Benzaldehyde and its Behaviour with Sulphuric Acid. By RICHARD REIK (*Monatsh.*, 1897, 18, 598—612).—The author finds that the glycol

obtained by the condensation of isobutaldehyde with benzaldehyde (Fossek and Swobada, *Abstr.*, 1891, 31), is a 3-phenyl-2:2-dimethylpropane-1:3-diol, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CHPh}\cdot\text{OH}$, as, on oxidising it with cold potassium permanganate solution, benzoic and acetic acids were obtained, together with phenylisopropyl ketone, which was characterised by its oxime.

On heating 3-phenyl-2:2-dimethylpropane-1:3-diol with 14 per cent. sulphuric acid, β -butenylbenzene (3-phenyl-2-methylpropene-2), $\text{CMe}_2\cdot\text{CHPh}$ (Perkin, *Trans.*, 1879, 136), is formed, along with a *methylene ether* of the glycol, $\text{CMe}_2\cdot\left\langle\begin{array}{c} \text{CH}_2-\text{O} \\ \text{CHPh}\cdot\text{O} \end{array}\right\rangle\text{CH}_2$. This substance

can also be prepared by the condensation of formaldehyde with the glycol, using Tollens' method; it is a white, crystalline substance which melts at 39° , and boils at 135° under 15 mm. pressure. The decomposition of the glycol is explained by Lieben in the following equations, it being assumed that formaldehyde is liberated in the first instance.



W. A. D.

Final Product of the Action of Nitrogen Chloride on Dimethylaniline. By W. HENTSCHEL (*Ber.*, 1898, 31, 246—249. Compare this vol., i, 130).—The product obtained by the action of nitrogen chloride on a benzene solution of dimethylaniline is shown to be $\text{C}_{24}\text{H}_{13}\text{Cl}_9\text{N}_2$, probably $\text{C}_6\text{H}_6\text{Cl}_5\cdot\text{N}(\text{C}_6\text{HCl}_4)\cdot\text{N}(\text{C}_6\text{HCl}_4)\cdot\text{C}_6\text{H}_5\text{Cl}_6$. It is best to saturate the solution first with hydrogen chloride, then with chlorine, and finally to add an excess of nitrogen chloride and to leave the mixture for several hours in the dark. An alcoholic solution of sodium ethoxide (12 atoms of sodium to 1 mol. of the compound) readily reacts with the product, yielding 2:3:4:6-tetrachloraniline and chlorinated phenols. Boiling alcohol also decomposes the compound, yielding methylamine hydrochloride and symmetrical trichlorophenol, together with other substances. Zinc dust and acetic acid react with the compound, yielding trichlormethylaniline.

J. J. S.

Action of Trimethylamine, Dimethylamine, and Methylamine on Bromacetophenone. By HANS RUMPEL (*Chem. Centr.*, 1897, i, 494—495; from *Diss. Marburg*, 1897).—According to the author, bromacetophenone is best prepared by the action of bromine on acetophenone in aqueous solution. By the action of trimethylamine on this compound, *phenacyltrimethylammonium bromide*, $\text{NMe}_3\text{Br}\cdot\text{CH}_2\text{Bz}$, is formed; it melts at 207° , is easily soluble in alcohol and in water, but almost insoluble in ether. The aurochloride crystallises in characteristic dark-brown leaflets of variable composition. The oxime is very soluble in water and alcohol, but insoluble in ether and light petroleum. By the action of sodium amalgam on the bromide, hydrogen bromide, trimethylamine, and an oily substance, which is perhaps phenylmethylcarbinol, are formed. Neither fuming hydrochloric acid nor sodium carbonate has any action on the bromide at 150° , but sodium hydroxide decomposes it into trimethylamine and benzoic acid.

The corresponding *chloride*, obtained by the action of silver chloride

on the bromide, melts at 202° ; the *aurochloride* at 180 — 181° , the *platinochloride* at 235 — 240° , the *mercurochloride* at 205° , and the copper double salt at 200 — 201° . The *oxime* obtained from the chloride melts at 186° , and forms an *aurochloride* and a *platinochloride* which melt at 147 — 148° and 199 — 201° respectively, and cannot be recrystallised owing to decomposition. The oxime is not attacked by acetic chloride or acetic anhydride, but is decomposed by 25 per cent. hydrochloric acid or by concentrated sulphuric acid, with formation of hydroxylamine and the corresponding salt of phenacyltrimethylammonium. On reduction with sodium amalgam, the oxime yields trimethylamine and *a*-phenylethylamine. Phosphorus pentachloride brings about a molecular rearrangement, forming $\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$; the *platinochloride* of this compound decomposes at 210 — 215° , and the *aurochloride* melts at 174 — 175° ; both these salts are more stable than the oxime itself.

By the action of dimethylamine on bromacetophenone, *phenacyldimethylamine hydrobromide*, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{COPh}\cdot\text{HBr}$, and *diphenacyldimethylammonium bromide*, $\text{NMe}_2\text{Br}(\text{CH}_2\text{Bz})_2$, are formed; the former crystallises in nodules, melts at 184 — 186° , is very easily soluble in cold water, and yields a *platinochloride* melting at 206° and an *aurochloride* melting at 158° , whilst the latter crystallises in needles, is slightly soluble in cold water, melts at 156° , and forms a *platinochloride* and an *aurochloride* which melt at 201 — 202° and 112 — 114° respectively.

By the action of methylamine on bromacetophenone, *phenacylmethylamine hydrobromide*, $\text{NHMe}\cdot\text{CH}_2\cdot\text{COPh}\cdot\text{HBr}$, and *diphenacylmethylamine hydrobromide*, $\text{NHMe}(\text{CH}_2\text{Bz})_2\cdot\text{HBr}$, are formed; the former crystallises in leaflets, is easily soluble in cold water, melts at 203° , and forms an *aurochloride* melting at 134° and a *platinochloride* melting at 200° . The latter crystallises in needles, is slightly soluble in cold water, and melts at 229 — 230° . Its *aurochloride* melts at 240° and the *platinochloride* at a higher temperature. Strychnine acetophenone bromide (Abstr., 1897, i, 644—645) decomposes at 160° ; the *aurochloride* of the corresponding chloride melts at 190 — 193° , and the *platinochloride* at 220 — 222° .

E. W. W.

The so-called Nitramines and Isonitramines and their Ethers.

By ARTHUR R. HANTZSCH (*Ber.*, 1898, 31, 177—187).—The nitramines yield two isomeric methylic ethers, in one of which the alkyl group is combined with nitrogen and in the other with oxygen. The isonitramines, in a similar manner, yield two isomeric ethers, but both of these are oxygen ethers, one being derived from nitrosohydroxylamine, whilst the constitution of the second is unknown.

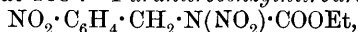
Nitramine, $\text{R}\cdot\text{NH}\cdot\text{NO}_2$; nitrogen ether, $\text{R}\cdot\text{NMe}\cdot\text{NO}_2$; oxygen ether of unknown constitution, $\text{R}\cdot\text{N}_2\text{O}\cdot\text{OMe}$.

Isonitramine, $\text{R}\cdot\text{N}(\text{OH})\cdot\text{NO}$; nitrosohydroxylamine ether, $\text{R}\cdot\text{N}(\text{OMe})\cdot\text{NO}$; oxygen ether of unknown constitution, $\text{R}\cdot\text{N}_2\text{O}\cdot\text{OMe}$.

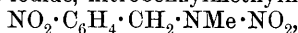
In endeavouring to prepare all the four isomeric derivatives corresponding with phenylnitramine and isonitramine, the author found that only the already known ether of the isonitramine could be obtained, but he succeeded in preparing four methyl ethers derived from paranitrobenzyl nitramine and the corresponding isonitramine.

Benzylurethane (ethylic benzylcarbamate) has already been

described by Cannizzaro, who, however, gives the melting point as 86° , whilst the author finds it to be $48-49^{\circ}$. It was found impossible to prepare benzylnitro-urethane from this compound, whereas *paranitrobenzylurethane*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{COOEt}$, can readily be obtained from it and melts at 118° . *Paranitrobenzylnitrourethane*,

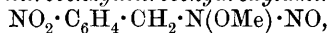


is formed by the action of pure nitric acid on benzylurethane and yields *paranitrobenzylnitramine*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}_2\text{O}_2\text{H}$, on treating it with ammonia in ethereal solution and acidifying; this nitramine melts at 116° and yields white, crystalline salts with dilute alkalis, which yield the original nitramine when acidified. When the sodium salt is treated with methylic iodide, nitrobenzylmethylnitramine,



the nitrogen ether is formed and is identical with the product melting at 72° obtained by Franchimont (*Rec. trav. chim.*, 14, 246), from methylnitramine and paranitrobenzylic chloride. The isomeric *oxygen ether*, obtained by the action of methylic iodide on the silver salt, crystallises in long needles melting at $115-116^{\circ}$ and when heated with alcoholic hydrogen chloride passes into the nitrogen ether melting at 72° .

Nitrobenzylisonitramine, when etherified by the action of methylic iodide on its silver salt, yields two isomeric ethers; that formed in smaller quantity is *nitrobenzylnitrosohydroxylamine methyl ether*,



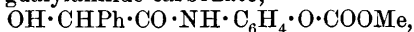
which melts at 26° , gives Liebermann's reaction with phenol and sulphuric acid, and is identical with the product obtained from α -methylhydroxylamine and paranitrobenzylic iodide. The *isomeride*, however, which is the chief product, is still of unknown constitution, and crystallises in well-developed needles melting at $145-146^{\circ}$. Nitrobenzylnitramine, the corresponding isonitramine, and the two isomeric oxygen ethers of uncertain constitution are all decomposed by concentrated sulphuric acid with formation of paranitrobenzylic alcohol and its sulphonic acid. The oxygen ether of nitrobenzylnitramine is decomposed in the cold by alcoholic potash, nitrous oxide being evolved and nitrobenzylic alcohol produced, whilst the isonitramine derivative simply yields a deep violet-coloured solution, which changes colour when heated but has not yielded any definite products of decomposition.

An unsuccessful attempt was also made to ascertain the probable formulæ of the two oxygen ethers of uncertain constitution by a study of their physical properties; it was, however, found that, whilst they have identical molecular refractions, the nitramine derivative has a somewhat greater molecular volume in solution than the isonitramine compound. The unetherified nitramine and isonitramine, on the other hand, have identical molecular volumes in solution. No adequate explanation of the isomerism of these two oxygen ethers has therefore yet been found.

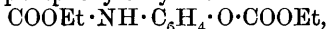
A. H.

Action of Phosgene and of Ethylic Chloroformate on Paracetamidophenols and on Parahydroxyphenylurethanes. By C. EMANUEL MERCK (*Chem. Centr.*, 1897, i, 468-469; from *Ber. ii. d. Jahr.*, 1896, 5-11).—By the action of phosgene gas and of ethylic

chloroformate respectively on paracetamidophenol, *paradiacetanilide carbonate*, $(\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2\text{CO}$, and *ethylic paracetanilide carbonate*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOEt}$, are formed; the former crystallises in leaflets, melts at about 200° , and is slightly soluble in water and easily in alcohol, the latter crystallises from alcohol in needles, melts at 120° and is very slightly soluble in water. Parahydroxyphenylurethanes undergo similar reactions with phosgene and ethylic chloroformate. By means of these reactions, the author has prepared the following compounds, parapropanilide carbonate, $\text{CO}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_3\text{H}_5\text{O})_2$, crystallises from alcohol, melts at 180° , and is slightly soluble in water; parabenzoylanilide carbonate, $\text{CO}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NHBz})_2$, a fine, crystalline powder, melts and decomposes at 220° ; it is slightly soluble in ether, almost insoluble in alcohol and in water; paraphenylethylurethane carbonate, $\text{CO}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{COOEt})_2$, forms white leaflets, melts at 184° , and is easily soluble in alcohol, very slightly in water; paraphenylpropylurethane carbonate, $\text{CO}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{COOPr})_2$, forms white leaflets, melts at 155° , and is slightly soluble in water, easily in ether; propylic paracetanilide carbonate, melts at $105\text{--}108^\circ$, and is very slightly soluble in water; butylic paracetanilide carbonate forms lustrous crystals and melts at $117\text{--}120^\circ$; ethylic parapropanilide carbonate, $\text{COEt} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOEt}$, forms needles or plates, melts at $101\text{--}103^\circ$, and is slightly soluble in water; ethylic parabenzanilide carbonate, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOEt}$, crystallises in needles, melts at $183\text{--}184^\circ$, and is slightly soluble in alcohol, but insoluble in water; phenylglycolylparamidophenylic methylic carbonate or methylic amygdalylanilide carbonate,



melts at $135\text{--}136^\circ$, is very slightly soluble in water, easily in alcohol; phenylglycolylparamidophenylic ethylic carbonate or ethylic amygdalylanilide carbonate, known in commerce as amygdophenin, melts at $162\text{--}163^\circ$; ethylic paraphenylethylurethane carbonate,



forms lustrous needles, melts at $104\text{--}105^\circ$, and is very slightly soluble in water, easily in alcohol; ethylic paraphenylpropylurethane carbonate, $\text{COOPr} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOEt}$, forms white plates, melts at $94\text{--}96^\circ$, and is very slightly soluble in water; propylic paraphenylethylurethane carbonate, $\text{COOEt} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOPr}$, melts at $54\text{--}56^\circ$, and is slightly soluble in water.

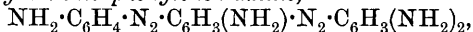
E. W. W.

Electro-Chemical Introduction of Hydroxyl Groups into Azobenzene. By JOHANN HEILPERN (*Zeit. Elektrochem.*, 1897, 4, 89—90).—Azobenzene, dissolved in the smallest quantity of concentrated sulphuric acid, is placed in a porous cell containing the anode, the cathode is immersed in a fairly concentrated solution of caustic potash or of potassium chromate surrounding the porous cell, and a current of 3 to 4 ampères passed for 5 hours; the greenish-black precipitate formed is purified by dissolution in caustic soda and precipitation by hydrochloric acid. The tetrahydroxyazobenzene thus obtained is, when dry, a dark green, amorphous mass, soluble in alkalis or concentrated sulphuric acid with a cherry-red colour, and in glacial acetic acid with a yellow colour; water precipitates it from acid solu-

tions as a dark-red precipitate; 5 grams of azobenzene yield 5 grams of the product. The tetracetyl derivative was obtained in the form of reddish-yellow needles, readily soluble in alcohol and ether, and melting at 240—242°. The substance strongly resembles the parazonophenolphloroglucinol described by Benedict and Weselsky (*Ber.*, 1879, 12, 227); it dyes wool and silk yellow, the colour being fast to light, soap, and acids.

T. E.

Disazo-compounds from Metaphenylenediamine. By KARL EIERMANN (*Ber.*, 1898, 31, 188—191).—The author has synthesised two isomeric disazo-compounds from metaphenylenediamine, and since neither of them is identical with that obtained from Bismarck-brown by Täuber and Walder, it follows that the constitution assigned by these authors to their compound is correct. *Metamidophenylazo-metamidophenylazo-metaphenylenediamine*,



can be obtained by the following series of operations. Monacetylmetaphenylenediamine readily yields a diazo-solution, which reacts with another molecule of the monacetyl derivative to produce an *amidoazo-compound*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{NHAc}$; this forms golden-yellow, crystalline flakes melting at 229—230°, and when heated with hydrochloric acid yields triamidoazobenzene. This compound is again converted into a diazo-compound, metaphenylenediamine is added, and the diacetyl derivative of the disazo-compound thus formed, when hydrolysed with hydrochloric acid, finally yields the required substance. The disazo-compound prepared in this way separates from benzene, or a mixture of benzene and phenol, in red, lustrous crystals of the formula $3\text{C}_{18}\text{H}_{18}\text{N}_8 \cdot 2\text{C}_6\text{H}_6$, and melts, when free from benzene, at 134°. The isomeric *bis-metamidophenylazo-metaphenylenediamine*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_2(\text{NH}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, is prepared by acting with metaphenylenediamine (1 mol.) on diazotised monacetylmetaphenylenediamine (2 mols.), and heating the product with hydrochloric acid. It separates from benzene or a mixture of benzene and phenol in reddish-yellow crystals of the composition $\text{C}_{18}\text{H}_{18}\text{N}_8 + \text{C}_6\text{H}_6$, which, when pure, melts at 116—118°.

A. H.

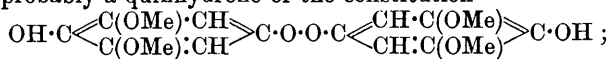
Influence of Methoxyl Groups in Diazotising Aromatic Compounds. By PIETRO BIGINELLI (*Gazzetta*, 1897, 27, ii, 347—357).

—A *dinitromethoxycoumarin*, $\text{OMe} \cdot \text{C}_6\text{H}(\text{NO}_2)_2$ $\begin{matrix} \text{O} - \text{CO} \\ \diagup \quad \diagdown \\ \text{CH} : \text{CH} \end{matrix}$, is obtained on dissolving Tiemann's methoxycoumarin in cooled fuming nitric acid and pouring the product on to ice; it crystallises in yellow needles melting at 149—150°. On reduction with iron filings in acetic acid solution, it yields an *amido-derivative*, $\text{OMe} \cdot \text{C}_6\text{H}(\text{NH}_2)_2$ $\begin{matrix} \text{O} - \text{CO} \\ \diagup \quad \diagdown \\ \text{CH} : \text{CH} \end{matrix}$ which crystallises in needles or scales melting at 227—228°, and is insoluble in dilute hydrochloric acid; when diazotised, it gives a black, infusible substance which is not decomposed by long boiling with dilute sulphuric acid. On diazotising Nietzki and Preusser's diacetamidoquinol (*Abstr.*, 1886, 1024; 1887, 574), a similar black, infusible

substance is obtained, so that the peculiar behaviour of the coumarin derivative towards nitrous acid is not due to its containing the coumarin chain.

By varying the conditions under which methoxycoumarin is nitrated, a *mononitromethoxycoumarin*, $C_{10}H_7NO_5$, may be obtained; it crystallises in yellow needles melting at $155-156^\circ$. On reduction with iron in acetic acid solution, this yields a *monamidomethoxycoumarin*, $C_{10}H_9NO_3$, crystallising in prisms which exhibit a blue fluorescence and melt at $222-223^\circ$; its *acetyl* derivative, $C_{11}H_{12}NO_4$, crystallises in yellow prisms melting first at $207-208^\circ$, and after fusion at $211-212^\circ$. On diazotising either the base or the acetyl derivative, a red, infusible *substance* difficult to purify is obtained. A small, relatively pure, portion of this contained nitrogen in quantity corresponding with the composition $C_{20}H_{15}NO_7$; it is soluble in dilute soda, and is precipitated by carbonic anhydride, showing that the coumarin linking still persists.

On diazotising the trimethyl ether of monamidopyrogallol, it yields a *substance*, $C_{16}H_{18}O_8$, crystallising in needles and melting at $243-244^\circ$; this is probably a quinhedrone of the constitution

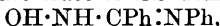


it is accompanied by a *substance* which probably has the constitution $OMe \cdot C \begin{array}{c} \swarrow C(OMe) \cdot CH \\ \searrow C(OMe) : CH \end{array} > C \cdot NH \cdot O \cdot C \begin{array}{c} \swarrow CH \cdot C(OMe) \\ \searrow CH : C(OMe) \end{array} > COMe$ being insoluble in soda, and unaltered by boiling with dilute sulphuric acid.

It is concluded that, in cyclic compounds, the presence of methoxyl groups impedes diazotisation, and that during the diazotisation of such compounds, condensation products are mainly formed.

W. J. P.

Action of Hydroxylamine Derivatives on Imidochlorides. By HEINRICH LEY (*Ber.*, 1898, 31, 240-246).—Tiemann's benzenyl-anilidoxime, $OH \cdot N : CPh \cdot NPh$, is obtained by the action of hydroxylamine on benzanilidoimidochloride. The requisite quantity of sodium ethoxide (from 3.8 grams of metal) is added to a solution of hydroxylamine hydrochloride (11.5 grams) in absolute alcohol. The hydroxylamine solution, after the removal of the sodium chloride, is added to a solution of benzanilidoimidochloride (14 grams) in absolute alcohol, and the mixture allowed to remain for several hours. The solvent is then distilled off, and the product precipitated with water; after recrystallisation from dilute alcohol, it melts at 138° (Müller, *Abstr.*, 1886, 875, gives 136°). No trace of the isomeric compound,



is formed.

Stieglitz's benzenylorthotoluidoxime may be obtained in a similar manner from benzorthotoluidimidochloride.

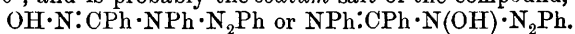
Benzenylparachloranilidoxime crystallises in colourless needles or plates, melts at 183° , and gives a blue coloration with ferric chloride. It is readily soluble in acetone or hot alcohol, and only sparingly in light petroleum.

Parachlorobenzanilidimidochloride crystallises in long needles melting

at 68°. The *imidochloride* from benzoylorthonitraniline melts at 67—68°, and yields an *oxime* crystallising in yellow plates which melt and decompose at 187°. α -Benzylhydroxylamine reacts with benzanilid-imidochloride, yielding the same product as is formed when benzenylanilidoxime is benzylated.

β -Benzylhydroxylamine, in perfectly neutral absolute alcoholic solution, also reacts with benzanilidimidochloride; the crystalline product $\text{NPh}:\text{CPh}\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{OH}$, after being freed from oil and recrystallised from dilute alcohol or benzene, forms small, white, glistening needles melting at 148°. Its alcoholic solution gives a deep blue coloration with ferric chloride, and its ethereal solution a brownish-red. The oximes described above show the same colorations with ferric chloride. The compound exhibits many of the properties of Bamberger's azohydroxyamides.

Stieglitz (Abstr., 1890, 254) has previously shown that diazonium salts do not react with anilidoximes; the author finds that a reaction readily takes place in alkaline solution. Aniline (0.9 gram) is dissolved in normal hydrochloric acid (25 c.c.) and diazotised with the requisite quantity of sodium nitrite, and the strongly cooled diazonium solution is added to a solution of benzenylanilidoxime (2 grams) in excess of sodium hydroxide and kept at -5° . The yellow precipitate thus obtained may be recrystallised from alcohol, but the greater part undergoes decomposition during the process; it forms minute needles decomposing at 155—160°, and is probably the *sodium* salt of the compound,



It dissolves in acids, yielding colourless solutions, but is probably hydrolysed at the same time. J. J. S.

Stability of the Six Xylylsuccinimides. By ARTURO MIOLATI and ALFREDO LOTTI (*Real. Accad. Linc.*, 1896, [v], 5, i, 88—96).—The authors have determined the velocity constants Ac , of hydrolysis of the isomeric xylylsuccinimides, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N} \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$, by soda, with the results summarised in the accompanying table; these substances, which have not previously been prepared, boil at above 300° without decomposition, and crystallise well.

$\text{Me} : \text{Me} : \text{N}(\text{CO}\cdot\text{CH}_2)_2$	Ac .	Melting point.
1 : 3 : 2	0.1571	187°
1 : 2 : 3	0.8147	105
1 : 3 : 4	0.8653	118
1 : 4 : 5	0.8757	120
1 : 3 : 5	1.145	168
1 : 2 : 4	1.270	150

The imides can be divided into three groups according to the above velocity constants. The first group consists of the 1 : 3 : 2 isomeride, which has a small velocity constant, and in which both methyl groups are in ortho-positions relatively to the imido-group; the second group consists of the 1 : 2 : 3, 1 : 3 : 4, and 1 : 4 : 5 isomerides, which have

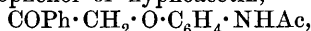
velocity constants of the same order, and in these one methyl group is ortho- to the imidogen; in the third group, consisting of the 1:3:5 and 1:2:4 derivatives, no methyl group is in the ortho-position relatively to the imido-group, and these have appreciably higher velocity constants.

W. J. P.

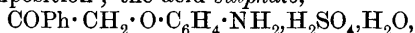
Condensation Products of Piperonal, Vanillin, and Protocatechuic Aldehyde. By M. ROGOFF (*Ber.*, 1898, 31, 175—176).—Piperonal, vanillin, and protocatechuic aldehyde readily form condensation products with amidophenols and their ethers. The *product* obtained from piperonal and paramidophenol is a crystalline powder melting at 208—209°, whilst that from paranisidine crystallises in colourless needles and melts at 121°. Vanillin and paramidophenol yield a *compound* which is a brown, crystalline powder melting at 203°, whilst the *product* obtained from paranisidine crystallises in colourless prisms and melts at 137°. The product from protocatechuic aldehyde and paramidophenol has not yet been obtained pure, but the corresponding compound with paranisidine forms glistening, golden-yellow crystals, and melts at 161—161·5°.

A. H.

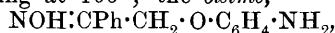
Base of Hypnoacetin and its Derivatives. By G. VIGNOLO (*Real. Accad. Linc.*, 1897, [v], 6, i, 70—77 and 122—127).—Acetophenoneparacetamidophenol or hypnoacetin,



(*Abstr.*, 1897, i, 617), is prepared by heating, in a reflux apparatus, a mixture of an alcoholic solution of monobromacetophenone with a solution of paracetamidophenol in alcoholic potash, hypnoacetin separating on cooling. It crystallises in transparent, six-sided scales, melting and decomposing at 160°, and is hydrolysed by hot hydrochloric acid with production of *acetophenoneparamidophenol*, $\text{COPh} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, which separates on adding alkali, and crystallises in fine needles melting at 95°; its *hydrochloride*, which separates on boiling hypnoacetin with hydrochloric acid, crystallises in fine needles melting at 201° with decomposition; the acid *sulphate*,

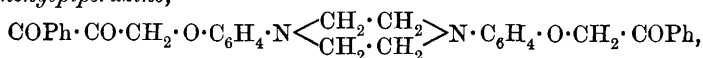


crystallises in prisms melting and decomposing at 188° and the normal *sulphate* crystallises, with $1\text{H}_2\text{O}$, in thin scales melting at 210°. The *nitrate* crystallises in needles or laminæ melting and decomposing at 160°, whilst the *picrate* is a yellow, crystalline powder melting at 177°. The *benzoyl* derivative, $\text{COPh} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NHBz}$, crystallises in white needles melting at 166°; the *oxime*,

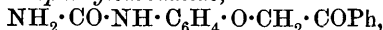


crystallises in needles and the *hydrazone* forms small, yellowish crystals melting at 128°.

On heating a mixture of acetophenoneparamidophenol, sodium acetate, and ethylenic dibromide in a reflux apparatus, at a temperature not higher than 145°, for 2 hours, extracting with water, and crystallising the residue from chloroform, *diparoxyacetophenone-diphenylpiperazine*,



is obtained as a white, crystalline powder melting at 175°.

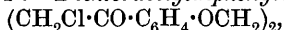
Paroxyacetophenonephenylcarbamide,

prepared by the action of potassium cyanate on acetophenoneparamidophenol hydrochloride in aqueous solution, crystallises in slender needles melting and decomposing at 160° ; it is tasteless, and is physiologically inactive.

Hypnoacetin administered internally to the human subject has an antipyretic action and analgesic and hypnotic properties; its effects, however, are not always uniform, and it is innocuous in doses of 0.25—1 gram per day.

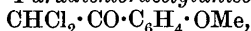
The physiological effects of acetophenoneparamidophenol administered hypodermically to animals have been investigated; it is rapidly eliminated in the urine. W. J. P.

Some Mono- and Di-halogen Ketones. By FRANZ KUNCHELL and FRIEDRICH JOHANNSEN (*Ber.*, 1898, 31, 169—172. Compare Abstr., 1897, i, 522).—Parahydroxychloracetophenone (parachloroacetylphenol), $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, cannot be obtained by the action of chloroacetic chloride on phenol, but is readily formed when anisole is treated with the chloride in presence of aluminium chloride; it crystallises in reddish plates, melts at 148° , and readily dissolves in dilute aqueous soda and in alcohol. *Paramethoxyphenacylparaphenetidine*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, formed by the action of anisyl chloromethyl ketone on phenetidine, crystallises in pale yellow plates melting at 124° ; by nitric acid, it is converted into a *mono-nitro*-compound, which crystallises in red plates and melts at 171° . *Parachloroanisyl chloromethyl ketone*, prepared from parachloroanisole, melts at 71° , whilst the corresponding *parabromoisyl chloromethyl ketone* crystallises in white needles melting at 94° . *Chloroacetylphenylic parabromomethyl ether*, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_2\text{H}_4\text{Br}$, prepared from phenylic bromomethyl ether, forms small, hard, yellowish-white crystals melting at 104° . *Dichloroacetyldiphenylic ethylenic ether*,



is prepared in a similar manner from diphenylic ethylenic ether, and forms a white mass melting at 160 — 165° .

Phenylic dichloroacetate, prepared by the action of dichloroacetic chloride on phenol in the presence of aluminium chloride, forms white plates melting at 33° . *Paradichloroacetylanisole*,



crystallises in colourless needles, melting at 75 — 76° , whilst *dichloroacetylphenetole* forms reddish plates melting at 73° . *Dichloroacetyl- α -naphthyl methyl ether*, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$, crystallises in long, white needles melting at 100° , whilst the corresponding ethyl ether crystallises in white, compact needles melting at 110° . A. H.

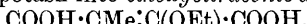
Some Brominated Ketones. By FRANZ KUNCHELL and WILHELM SCHEVEN (*Ber.*, 1898, 31, 172—174. Compare the foregoing abstract).—The following compounds have been obtained by acting on phenol and its ethers with bromoacetic bromide in the presence of aluminium chloride. *Phenylic bromoacetate*, $\text{CH}_2\text{Br} \cdot \text{COOPh}$, crystallises in white, lustrous plates melting at 32° . Anisole yields *anisyl parabromomethyl ketone*, $\text{CH}_2\text{Br} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, which crystallises in white needles

melting at 73° , whilst if double the quantity of the bromide and aluminium chloride be employed, *anisyl di-bromomethyl diketone*, $(\text{CH}_2\text{Br}\cdot\text{CO})_2\text{C}_6\text{H}_3\cdot\text{OMe}$, is formed; this crystallises in yellowish-white needles melting at $79-80^{\circ}$; *phenetyl parabromomethyl ketone* also forms white needles and melts at $59-60^{\circ}$, whilst *phenetyl di-bromomethyl diketone* crystallises in hard, reddish needles melting at 77° . *Bromacetyl- α -naphthyllic methyl ether*, $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{OMe}$, crystallises in greenish needles melting at 70° , whilst the corresponding *ethyllic ether* forms yellowish-white needles and melts at 119° . A. H.

Action of Sodium Ethoxide on Ethylic $\alpha\beta$ -Dibromophenylpropionate, Ethylic Citradibromopyrotartrate, and Ethylic $\alpha\beta$ -Dibromopropionate. By VIRGIL L. LEIGHTON (*Amer. Chem. J.*, 1898, 20, 133—148).—This work is an extension of that of Michael and Bucher on the action of sodium ethoxide on ethylic dibromosuccinate (*Abstr.*, 1896, i, 85 and 599); when an excess of the former (20 per cent. more than that calculated for 2 mols. of sodium ethoxide) is left in contact, during 3 days, with ethylic $\alpha\beta$ -dibromophenylpropionate in alcoholic solution, small quantities of phenylpropionic acid and *ethylic diethoxyphenylpropionate*, $\text{CPh}(\text{OEt})_2\cdot\text{CH}_2\cdot\text{COOEt}$, are formed, together with a much larger proportion of *ethylic β -ethoxycinnamate*, $\text{OEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COOEt}$.

When slightly impure, ethylic diethoxyphenylpropionate boils at $146-148^{\circ}$ under 10 mm. pressure, and is converted by cold 4 per cent. alcoholic potash into benzoylactic acid. *Ethylic β -ethoxycinnamate* boils at $154-155^{\circ}$ under 9 mm. pressure, and is converted by boiling 4 per cent. alcoholic potash into *β -ethoxycinnamic acid*, which separates from carbon tetrachloride in slender, transparent crystals, and melts at $164-165^{\circ}$. The *silver* salt, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Ag}$, is a white, microcrystalline powder, whilst the *calcium* salt, with $8\text{H}_2\text{O}$, crystallises from water in white needles. On being left in contact with concentrated hydrochloric acid (sp. gr. = 1.2), both *β -ethoxycinnamic acid* and its ethylic salt are converted into benzoylactic acid.

When an excess (20 per cent. more than 2 molecular proportions) of sodium ethoxide is left in contact with ethylic citradibromopyrotartrate dissolved in alcohol, *ethylic ethoxycitraconate* is formed, together with a larger quantity of *ethylic diethoxypyrotartrate*. The former compound boils at 140° under 15 mm. pressure, and is converted by cold 4 per cent. alcoholic potash into *ethoxycitraconic acid*,



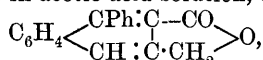
a thick, viscous oil; the *barium* salt, with H_2O , is precipitated on adding alcohol to its aqueous solution; the *ethyllic* salt, when boiled with 10 per cent. sulphuric acid, is converted into propionylformic acid. *Ethylic diethoxypyrotartrate*, $\text{COOEt}\cdot\text{CH}(\text{OEt})\cdot\text{CMe}(\text{OEt})\cdot\text{COOEt}$, boils at 157° under 15 mm. pressure, and is converted by dilute caustic potash into *diethoxypyrotartaric acid*, a thick oil, which yields a white, crystalline *silver* salt, $\text{C}_9\text{H}_{13}\text{O}_6\text{Ag}_2$, and an insoluble *lead* salt; all the other metallic salts are very soluble in water.

When alcoholic sodium ethoxide reacts with ethylic $\alpha\beta$ -dibromopropionate, a mixture of *ethylic ethoxyacrylate* and *ethylic diethoxypropionate* is formed. W. A. D.

Action of Acetic Anhydride on Phenylpropionic Acid. By ARTHUR MICHAEL and JOHN E. BUCHER (*Amer. Chem. J.*, 1898, **20**, 89—120).—The action of acetic anhydride on phenylpropionic acid is not analogous to its action on acetylenedicarboxylic acid; whereas, in the latter case, acetoxymaleic anhydride is obtained (Abstr., 1896, i, 85), the former reaction yields 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride; this crystallises from cumene in transparent prisms, and, when heated, softens at 230° and melts at 255°. It dissolves in a boiling 10 per cent. solution of sodium hydroxide, and, on cooling, white, shining plates of sodium 1-phenylnaphthalene-2 : 3-dicarboxylate, $C_{18}H_{10}O_4Na_2 + 4\frac{1}{2}H_2O$, separate. The corresponding barium salt crystallises with $4H_2O$, and yields α -phenylnaphthalene when distilled with barium hydroxide; the calcium salt crystallises with $3H_2O$, whilst the silver salt is anhydrous, and is not affected by light. The methylic salt, $C_{16}H_{10}(COOMe)_2$, crystallises from alcohol in white prisms, melts at 118—120°, and is easily soluble in hot methylic and ethylic alcohols, and carbon tetrachloride, and less soluble in ether. No acid exists corresponding with these salts; on decomposing solutions of the metallic salts with acids, the anhydride, $C_{18}H_{10}O_3$, is immediately formed. By the action of aniline on this anhydride, a compound, $C_{18}H_{10}O_3.NH_2Ph$, is obtained, which separates from alcohol in transparent crystals and melts at 194° with decomposition.

On reducing sodium 1-phenylnaphthalene-2 : 3-dicarboxylate with sodium amalgam, and subsequently acidifying the solution with sulphuric acid, an acid, $C_{18}H_{16}O_4$, is obtained; this forms white crystals, melts and decomposes at 200—202°, and is easily soluble in acetone and ethylic acetate, but insoluble in carbon tetrachloride and benzene, and probably has the constitution of a 1-phenyltetrahydronaphthalene-2 : 3-dicarboxylic acid. The silver salt, $C_{18}H_{14}O_4Ag_2$, is a white, crystalline powder; the anhydride, $C_{18}H_{14}O_3$, obtained by heating the acid with acetic anhydride, melts at 145—150°.

When the anhydride of 1-phenylnaphthalene-2 : 3-dicarboxylic acid is reduced by zinc dust in acetic acid solution, a lactone,



is obtained, which crystallises from alcohol and melts at 135—137°.

1-Phenylbenzene-2 : 3 : 5 : 6-tetracarboxylic acid, obtained on oxidising 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride with alkaline potassium permanganate, is a white, crystalline substance which has no definite melting point; the silver salt, $C_{12}H_6(COOAg)_4$, and the lead salt, are amorphous powders, insoluble in water; the barium salt, containing $8H_2O$, is crystalline, and is less soluble in hot water than in cold; the calcium salt is easily soluble in water; the methylic salt crystallises from carbon tetrachloride in large transparent rhombohedra, melts at 130—133°, and is soluble in hot alcohol and chloroform, whilst the benzylic salt is a white, crystalline substance which melts at 114—118°. The anhydride of the acid is a light yellow, crystalline compound, soluble in boiling xylene. When the barium salt is distilled with barium hydroxide, diphenyl is obtained.

An acid, apparently isomeric with the foregoing, is formed along with it when 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride is

oxidised by potassium permanganate; it is amorphous, and yields an amorphous *barium* salt, which is very soluble in water and is converted into diphenyl when distilled with barium hydroxide; the *silver* salt, $C_{12}H_6(COOAg)_4$, and the *methylic* salt, $C_{12}H_6(COOMe)_4$, are also both amorphous. The constitution of the acid is uncertain, and its formation cannot be explained by theory.

In the light of the above results, the authors discuss the formation of the isotropic acids from atropic acid; this appears to be analogous to the formation of 1-phenylnaphthalene-2:3-dicarboxylic acid from phenylpropionic acid. The analogy supports the view taken by Fittig (Abstr., 1881, 425), that the isotropic acids are 1-phenyltetrahydronaphthalene-1:4-dicarboxylic acids. The constitution of atronic and isotronic acids is discussed; to atronol, the constitution of a dihydronaphthalene is attributed, whilst atronylene and its sulphonic acid are considered to be α -phenylnaphthalene and its sulphonic acid respectively.

W. A. D.

Action of Caustic Alkalis on Phthalides. By PIETRO GUCCI (*Real. Accad. Linc.*, 1897, [v], 6, i, 295—298).—On gradually heating diethylphthalide with caustic soda and a little water to 300° , diethyl ketone distils, whilst sodium benzoate with a little phthalate remains in the residue; with caustic potash, a better yield of the phthalate and a poorer one of the ketone is obtained. Diethylphthalide, therefore, behaves like dimethylphthalide towards caustic alkalis.

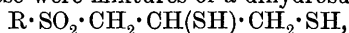
W. J. P.

Dimorphism of α -Monomethylic Hemipinate. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, 18, 589—597).—The more stable modification at ordinary temperatures melts at 138° . From ether, anorthic crystals were obtained containing $1H_2O$; these melted at 134.5 — 136.5° , and gave $a:b:c = 0.9105:1:1.0269$; $\alpha = 112^\circ 27'$, $\beta = 102^\circ 2'$, $\gamma = 95^\circ 25'$. When crystallised from water, this modification is converted into the one which melts at 120 — 122° , but this form, on being rubbed with a trace of the compound of higher melting point, is reconverted into the modification which melts at 138° . The two forms are apparently enantiotropic. Anorthic crystals containing $1H_2O$, were grown from an ethereal solution of the substance containing a crystal of the modification of lower melting point. They melted at 118 — 120° , and gave $a:b:c = 0.9342:1:0.9941$; $\alpha = 107^\circ 45'$, $\beta = 101^\circ 50'$, $\gamma = 107^\circ 40'$. Both modifications give the same reaction with ferric chloride.

W. A. D.

Action of Alcoholic Potassium Sulphide and Hydrosulphide on Symmetrical Dibromosulphones. By JULIUS TROEGER and V. HORNING (*J. pr. Chem.*, 1897, [ii], 56, 445—469).—The dibromide, $R \cdot SO_2 \cdot CH_2 \cdot CHBr \cdot CH_2 \cdot Br$, was usually mixed with a little alcohol, treated with excess of a strong alcoholic solution of potassium sulphide (1 c.c. = $0.225 K_2S$) or hydrosulphide, and the mixture either allowed to remain or heated on the water bath. With potassium sulphide, a sulphide, $R \cdot SO_2 \cdot CH_2 \cdot CH < \begin{smallmatrix} S \\ | \\ CH_2 \end{smallmatrix}$, was formed, as a rule; and this, in

acetic acid solution, could be oxidised by potassium permanganate to a disulphone, $R \cdot SO_2 \cdot CH_2 \cdot CH < \begin{smallmatrix} SO_2 \\ | \\ CH_2 \end{smallmatrix}$. With potassium hydrosulphide, impure yellow or reddish oils were obtained, and it was impossible to decide whether these were mixtures of a dihydrosulphide,



with a sulphide, or whether polymerisation had taken place. With amylic and phenylic hydrosulphides, in the presence of an equivalent amount of sodium ethoxide, they did react, yielding compounds of the type, $R \cdot SO_2 \cdot CH_2 \cdot CH(SR^1) \cdot CH_2 \cdot SR^1$, which could be oxidised to trisulphones, $R \cdot SO_2 \cdot CH_2 \cdot CH(SO_2 \cdot R^1) \cdot CH_2 \cdot SO_2 \cdot R^1$; these compounds were all oils, except $SO_2Ph \cdot CH_2 \cdot CH(SPh) \cdot CH_2 \cdot SPh$, which is crystalline (Otto, Abstr., 1895, i, 230). The dibromides experimented with were those of phenylallyl-, paratolylallyl-, orthotolylallyl-, β -naphthylallyl-, and α -naphthylallyl-sulphones [$R = Ph$; C_6H_4Me ; $C_{10}H_7$]. In the one case of phenylallylsulphone dibromide and potassium sulphide, the reaction is abnormal; the product, which melts at $157-158^\circ$, appears to have the constitution $\left[SO_2Ph \cdot CH_2 \cdot CH < \begin{smallmatrix} S \\ | \\ CH_2 \end{smallmatrix} \right]_2 O$; when

oxidised, it yields the disulphone, $SO_2Ph \cdot CH_2 \cdot CH < \begin{smallmatrix} SO_2 \\ | \\ CH_2 \end{smallmatrix}$, a crystalline powder which is still unmelted at 230° . The well-characterised substances obtained in the investigation are enumerated below, with their melting points; of those obtained only as oils, no further mention is made.

Phenylallyl derivatives.— $(SO_2Ph \cdot C_3H_5 \cdot S)_2O$, $157-158^\circ$;

$SO_2Ph \cdot C_3H_5 \cdot SO_2$,
above 230° ; $SO_2Ph \cdot C_3H_5(SO_2 \cdot C_3H_5)_2$, 120° . *Paratolylallyl derivatives*.
— $C_6H_4Me \cdot SO_2 \cdot C_3H_5 \cdot S$, $180-181^\circ$; $C_6H_4Me \cdot SO_2 \cdot C_3H_5 \cdot SO_2$, above
 200° ; $C_6H_4Me \cdot SO_2 \cdot C_3H_5(SO_2 \cdot C_3H_5)_2$, $112-113^\circ$;

$C_6H_4Me \cdot SO_2 \cdot C_3H_5(SO_2Ph)_2$,
 88.5° . *Orthotolylallyl derivatives*.—None well characterised. *β -Naphthylallyl derivatives*.— $C_{10}H_7 \cdot SO_2 \cdot C_3H_5 \cdot S$, amorphous;

$C_{10}H_7 \cdot SO_2 \cdot C_3H_5(SO_2 \cdot C_3H_5)_2$,
 136° . *α -Naphthylallyl derivatives*.— $C_{10}H_7 \cdot SO_2 \cdot C_3H_5 \cdot S$, amorphous.

C. F. B.

Condensation Products of Aldehydes with Phenols and Phenolic Acids. By LEOPOLD KAHL (*Ber.*, 1898, 31, 143—151).—Baeyer and others have shown that formaldehyde reacts with phenols in the proportion of one molecule of aldehyde to two of the phenol.

Caro's methylenedipyrogallol (Abstr., 1892, 856) is best obtained by the following method. A solution of pyrogallol (50 grams) in water (250 c.c.) is mixed with 15 grams of a 40 per cent. solution of formaldehyde, and concentrated hydrochloric acid (about 125 c.c.) is added to the mixture until no further precipitate is obtained, care being taken that the whole is well stirred. When the dry compound is dissolved in about 10 times its weight of concentrated sulphuric acid, kept in a stoppered vessel for 24 hours, and then exposed to the air in an open dish, *formopyrogallaurin*,

$\text{O}:\text{C}_6\text{H}_2(\text{OH})_2:\text{CH}\cdot\text{C}_6\text{H}_2(\text{OH})_3$ [$\text{O}:(\text{OH})_5 = 4:3:5$; $3':4':5'$], is deposited in the form of black, opaque, crystalline aggregates. It is best purified by dissolving it in boiling water and precipitating with hot, alcoholic hydrogen chloride. It readily dissolves in alkalis, yielding green solutions, and in alkali carbonates, yielding brown solutions.

A compound, $\text{C}_{16}\text{H}_{16}\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$, is obtained when a solution of pyrogallol (50 grams) in water (200 c.c.) is mixed with acetaldehyde (8.8 grams) and hydrochloric acid (125—150 c.c.), and then warmed on the water bath until no further precipitate is obtained. When recrystallised from 50 per cent. alcohol, it forms colourless needles or prisms sparingly soluble in absolute alcohol, ether, acetone, methylic alcohol, and ethylic acetate, and dissolves slowly in alkali carbonates, readily in alkalis, but not in concentrated sulphuric acid; when heated, it decomposes without melting, and does not yield a dye.

Methylenedinetaphthoresorcinol, $\text{CH}_2[\text{C}_{10}\text{H}_5(\text{OH})_2]_2$, after drying at 130° , forms a colourless, crystalline powder, composed of irregular plates; it crystallises from boiling water in needles, melts at 164.5° , and is readily soluble in alcohol, ether, acetic acid, or alkalis. It dissolves in cold, concentrated sulphuric acid, yielding *formaldehydehydroxynaphthofluorone*, $\text{O}:\text{C}_{10}\text{H}_5\begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}:\text{C}_{10}\text{H}_5\cdot\text{OH}$, which is deposited, as the solution becomes dilute, in the form of small, opaque, brownish crystals; this may be purified by recrystallisation from acetic acid, in which it dissolves, yielding a yellow solution with a green fluorescence, but it is insoluble in ether, benzene, or acetone.

A theoretical yield of methylenedisalicylic acid is obtained by Geigy and Co.'s method (D. R. P. No. 49970); it can readily be obtained in crystalline form, is only sparingly soluble in water, but dissolves readily in alcohol or acetic acid. It melts at 242° (Geigy gives 238°). *Formaurindicarboxylic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_3\text{O}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{COOH}$, is obtained when the above acid, dried at 120° , is dissolved in 10 times its weight of cold sulphuric acid and the solution, while kept quite cold, is treated with nitrosulphonic acid in amount corresponding with 1 mol. N_2O_3 ; on pouring the product into cold water, the dye is deposited in the form of orange-coloured flocks. It is best purified by conversion into its colourless sulphurous acid derivative, which can then be decomposed by warming with dilute acids. The *calcium*, *barium*, and *aluminium* salts are insoluble in water. *Methylenedicrosotic acid* is obtained when orthocresotic acid (2 parts), 40 per cent. formaldehyde (1 part), and concentrated hydrochloric acid (8 parts) are heated on the water bath; it crystallises from alcohol or acetic acid in prisms, melts and decomposes at $276\text{--}277^\circ$, and is moderately soluble in ether.

When resorcylic acid (10 grams) is mixed with concentrated hydrochloric acid and acetaldehyde (1.42 grams), and the mixture allowed to remain for several days, a colourless, amorphous product, formed by the condensation of two molecules of the aldehyde with two of resorcylic acid and the removal of two molecules of water, is obtained. It is very sparingly soluble in water, more readily in alcohol, ether, acetic acid, or ethylic acetate, but cannot be obtained in a crystalline form; it decomposes when heated, but does not melt.

When gallic acid (100 grams) is covered with concentrated sulphuric acid and then treated with acetaldehyde (12.9 grams), condensation takes place slowly; at the end of 48 hours, the mixture is poured into water, the product boiled with water to remove unaltered gallic acid, and recrystallised several times from 50 per cent. alcohol. Prismatic crystals are thus obtained, which are soluble in alcohol, ether, alkalis, and alkali carbonates, and have the composition $C_{18}H_{14}O_9$.

Benzaldehyde and gallic acid yield a condensation product, $C_{28}H_{16}O_8$, which crystallises from 50 per cent. acetic acid in opaque, nodular crystals which are insoluble in water. J. J. S.

Products of the Action of Formaldehyde on Gallic Acid. By RICHARD MÖHLAU and LEOPOLD KAHL (*Ber.*, 1898, 31, 259—266. Compare Caro, *Abstr.*, 1892, 855).—Four methylenedigallic acids have been obtained by the action of formaldehyde on gallic acid.

(1) Sparingly soluble, crystalline methylenedigallic acid. Caro's method gives a 20 per cent. yield of this acid, but a 57 per cent. yield may be obtained by the following method. Hot concentrated hydrochloric acid (375 grams) and 40 per cent. formaldehyde solution (60 grams) are added to a hot solution of gallic acid (100 grams) in water (1125 grams) contained in a reflux apparatus and placed on a boiling water bath. The contents of the flask are kept well stirred during the mixing. When no more precipitate is formed, the mixture is cooled and filtered, the residue is well washed, boiled with water, and filtered while hot, and then washed with alcohol and ether to remove colouring matter. It is a light, crystalline powder which becomes strongly electric on rubbing, is extremely sparingly soluble in hot water, but dissolves somewhat more readily in dilute or absolute alcohol, from which it crystallises in long, white needles. Its alkaline solutions readily turn red on exposure to the air. When heated, it chars and decomposes without melting. The *anhydride*, $C_{15}H_{10}O_9$, probably $C_6H(OH)_3 \begin{smallmatrix} \text{---CH}_2\text{---} \\ \text{CO}\cdot\text{O}\cdot\text{CO} \end{smallmatrix} C_6H(OH)_3$, is formed when a saturated alcoholic solution of the acid is boiled for some time; and the acid is completely converted into this anhydride when heated with 95 per cent. alcohol (5 parts) for an hour at 105° in sealed tubes. The anhydride is insoluble in water, alcohol, or ether, but soluble in concentrated sulphuric acid, yielding a yellow solution, and also in alkalis or alkali carbonates.

(2) A readily soluble crystalline methylenedigallic acid is deposited in the form of long, white needles when the hot aqueous washings from acid No. 1 are allowed to stand for some time. A better yield is obtained when 100 grams of gallic acid, 40 grams of formaldehyde solution, and 1500 grams of dilute hydrochloric acid (1 of acid to 4 of water) are heated for an hour on a briskly boiling water bath; the crude acid is filtered, washed with cold water until free from hydrogen chloride, and then extracted with boiling water; the yield is 30—40 per cent. It is moderately soluble in boiling water, readily in alcohol and ether, and when boiled with a quantity of water insufficient to dissolve it, together with a few drops of concentrated hydrochloric acid, it yields

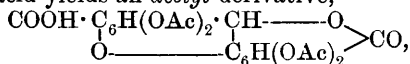
an *anhydride*, $C_{30}H_{22}O_{19}$, which can also be obtained by heating the acid with water at 110° for 2—3 hours; it forms large, reddish-coloured, rhombic crystals.

A readily soluble, amorphous methylenedigallic acid (No. 3) is deposited when the aqueous extracts from Caro's acid are allowed to remain for a week; it is also obtained when acid No. 2 is kept for several months in dilute hydrochloric acid solution. It is fairly readily soluble in hot water, very readily in alcohol, and dissolves in concentrated sulphuric acid, yielding a reddish-brown solution. Its phenylhydrazine salt is readily soluble in alcohol, but cannot be obtained in a crystalline condition from this solvent. When the acid is boiled for some time with alcohol, it is converted into the anhydride, $C_{15}H_{10}O_9$, which forms minute, prismatic crystals. It is insoluble in water and alcohol, but dissolves in alkalis, and is not identical with the anhydride obtained from Caro's acid.

A sparingly soluble, amorphous methylenegallic acid (No. 4) is readily obtained by Kleeberg's method (Abstr., 1891, 1199); the crude acid is digested several times with hot water, in order to remove acid No. 3. It is also obtained when acid No. 3 is heated with formaldehyde and hydrochloric acid on the water bath. It is very sparingly soluble in alcohol, acetone, acetic acid, and benzene, but dissolves in alkalis and alkali carbonates. The acid and also the anhydride, $C_{30}H_{22}O_{19}$, have been previously described by Baeyer (this Journal, 1873, 501) and by Kleeberg (*loc. cit.*), who, however, ascribed somewhat different compositions to them.

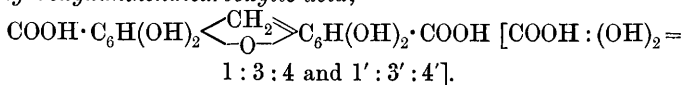
Acids Nos. 1 and 2 are readily converted into acid No. 3, and this in its turn into acid No. 4. J. J. S.

Formaldehydetrihydroxyfluoronedicarboxylic Acid. By RICHARD MÖHLAU and LEOPOLD KAHL (*Ber.*, 1898, 31, 266—271).—Ten grams of the sparingly soluble crystalline methylenedigallic acid (see previous abstract), previously dried at 100° , is dissolved in about 300 grams of concentrated sulphuric acid at a temperature below 70° , care being taken that the mass is kept well stirred; after cooling to the ordinary temperature, the requisite quantity of nitrosyl sulphate is added and the whole allowed to remain for 24 hours. The dye, $C_{15}H_8O_9$, may be obtained in a crystalline form by exposing the sulphuric acid solution to the atmosphere in flat dishes; it may also be precipitated by adding first diluted sulphuric acid (1:1) carefully so that the temperature does not rise above 35° , and then a still more dilute solution (1:10). It is a violet, crystalline powder, but sparingly soluble in boiling water, and practically insoluble in the usual solvents; it dissolves in concentrated sulphuric acid but does not yield a fluorescent solution. It forms sparingly soluble *lakes* with metallic oxides; *calcium* and *barium* salts form blue, flocculent precipitates. When heated with anhydrous sodium acetate and acetic anhydride, the acid yields an *acetyl* derivative,



which crystallises from alcohol in colourless, glistening plates melting at

140.5—141.5°; this is sparingly soluble in most solvents, dissolves to a colourless solution in sulphuric acid, but this gradually turns red, probably owing to hydrolysis. A *benzoyl* derivative, $C_{48}H_{24}O_{13}$, was also obtained by the aid of benzoic chloride; after dissolution in hot benzene and precipitation with hot alcohol, it forms large crystals melting at 250.5—252.5°. Formaldehydetrihydroxyfluoronedicarboxylic acid, when reduced with sodium carbonate and glucose, yields *tetrahydroxyxanthendicarboxylic acid*,



After several crystallisations from dilute alcohol (50 per cent.), it is obtained in spherical aggregates of prisms. Its solution in concentrated sulphuric acid turns cherry red on the addition of sodium hydroxide. When heated, it decomposes without melting, and when distilled with zinc dust yields xanthen. Its *tetracetyl* derivative, after recrystallisation from 50 per cent. acetic acid, forms glistening, colourless plates melting at 241°. J. J. S.

Phthaleins of Orthosulphobenzoic Anhydride. By M. D. SOHON (*Amer. Chem. J.*, 1898, 20, 127—129).—*Dimethylanilinesulphonphthalein*, $SO_2 \langle \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} \rangle C(C_6H_4 \cdot NMe_2)_2$, prepared by heating a mixture of dimethylaniline (2 mols.), orthosulphobenzoic anhydride (1 mol.), and phosphorus oxychloride on the water bath for a short period, is a bluish-black, brittle substance which dissolves in hot water giving a bright blue solution that dyes silk or wool the same colour. It is soluble in alcohol, but insoluble in ether, benzene, light petroleum, and chloroform; in dilute hydrochloric acid, it dissolves, giving a green solution which becomes yellow when excess of acid is added, and pink on the addition of alkali. The sulphonphthalein is not affected by reducing agents.

Diethylanilinesulphonphthalein possesses similar properties to those of the methyl compound. W. A. D.

Preparation of Phenylrosinduline. By LUDWIG PAUL (*Chem. Centr.*, 1897, i, 1168; from *Chem. Rund.*, 1897, 146—147).—The author describes the following new method of preparing phenylrosinduline. 5.8 grams of dry paranitrobenzeneazo- α -naphthylamine and 15 grams of aniline are kept at 160—165° for 2 hours in an oil bath, and the product boiled with dilute hydrochloric acid; the insoluble residue is then dissolved in boiling alcohol of 94° (Tralles), the solution filtered after 24 hours, and decomposed with sodium hydroxide solution. When purified by washing with alcohol of 50°, dissolving in alcohol of 94° and decomposing with sodium hydroxide, the phenylrosinduline melts at 229—230°.

If the above mixture is kept at 190—200° for 5 hours, the product obtained is not completely soluble in a solution of hydrochloric acid in alcohol, and gives a poorer yield of phenylrosinduline of a lower melting point and a bluer shade. By the action of 10 grams of aniline on 5 grams of benzeneazo- α -naphthylamine hydrochloride at 160° for 8

hours, only 2.5 grams of phenylrosinduline was obtained; it melted at 225° and had a darker colour (compare Fischer and Hepp, Abstr., 1888, 1291).
E. W. W.

Oxidation of Naphthalene by Potassium Permanganate. By JOSEPH TCHERNIAC (*Ber.*, 1898, 31, 139).—A reply to Procházka (this vol., i, 201). The author states that he has already given details for the oxidation of naphthalene by permanganate and also by manganate in his patent specifications.
J. J. S.

Naphthalene- and Orthotoluene-thiosulphonic Acids. By JULIUS TROEGER and W. GROTHE (*J. pr. Chem.*, 1897, [ii], 56, 470—475).—The potassium salts of these acids, $R \cdot SO_2 \cdot SK$, are obtained by adding the sulphonic chloride, $R \cdot SO_2Cl$, gradually to alcoholic potassium sulphide, warming at first; the solution is filtered from the potassium chloride and evaporated to crystallisation; it is difficult to obtain a product quite free from potassium chloride. The thiosulphonates of α - and β -naphthalene and of orthotoluene were prepared [$R = C_{10}H_7$; C_6H_4Me].
C. F. B.

Constituents of Oil of Roses and Allied Ethereal Oils. By JULIUS BERTRAM and EDUARD GILDEMEISTER (*J. pr. Chem.*, 1897, [ii], 56, 506—514).—A reply to H. Erdmann (this vol., i, 36, 37). It is shown that geraniol, as issued by Schimmel of Leipzig, does not contain chlorine compounds, and it is argued that *geraniol* is preferable to *rhodinol* as a name for the constituent $C_{10}H_{18}O$ common to oil of roses and oil of geranium.
C. F. B.

Rhodinol. By THEODOR POLECK (*Ber.*, 1898, 31, 29—30).—The author protests against the use of the term rhodinol for *l*-citronellol, $C_{10}H_{20}O$ (Tiemann and Schmidt, Abstr., 1896, i, 384); he had already applied it to a substance, $C_{10}H_{18}O$, which occurs in German and Turkish rose-oil (Abstr., 1891, i, 323).
C. F. B.

The Rhodinol Question. By THEODOR POLECK (*J. pr. Chem.*, 1897, [ii], 56, 515—519. Compare H. Erdmann, this vol., i, 37, and preceding abstract).—The use of *rhodinol* is advocated as a name for the constituent $C_{10}H_{18}O$ common to oil of roses and oil of geranium.
C. F. B.

Camphoronic Acid, Camphoranic Acid, and β -Hydroxycamphoronic Acid. By JULIUS BREDT (*Annalen*, 1897, 299, 131—160. Compare Abstr., 1896, i, 653).—Bromanhydrocamphoronic chloride (Abstr., 1895, i, 242) crystallises in the monosymmetric system; $a : b : c = 0.75904 : 1 : 0.78082$, $\beta = 87^\circ 53'$. α -Methylic bromanhydrocamphoronate crystallises in the rhombic system; $a : b : c = 0.91366 : 1 : 1.0434$. The β -methylic salt (m. p. 142°) separates from ether in crystals belonging to the same system; $a : b : c = 0.69502 : 1 : 0.42516$.

Dimethylic camphoranate separates from methylic alcohol in crystals belonging to the rhombic system; $a : b : c = 0.91153 : 1 : 0.70741$. The methylic hydrogen salt crystallises from water in the same system and contains $1H_2O$; $a : b : c = 0.6523 : 1 : 0.72565$. The anhydrous salt separates from ether in tetragonal crystals; $a : c = 1 : 1.9458$.

The paper gives a detailed account of compounds already described by the author (*loc. cit.*). M. O. F.

Isoacetophorone and Camphorone. By JULIUS BREDT and REINHARD RÜBEL (*Annalen*, 1897, 299, 160—192. Compare Kerp, Abstr., 1896, i, 447).—Kerp has shown that camphorone, the ketone, $C_9H_{14}O$, obtained by distilling calcium camphorate, is not identical with the isomeric substance produced from acetone under the influence of sodium ethoxide. The authors have independently arrived at the same conclusion, and find that the ketone has the same properties whether prepared by the action of quicklime or of sodium ethoxide. This ketone, which Kerp called isophorone, the authors refer to as *isoacetophorone*, with the double purpose of indicating its origin, and avoiding confusion with isocamphorone.

Isoacetophorone *phenylhydrazone*, $C_{15}H_{20}N_2$, crystallises from dilute alcohol in long, pale yellow needles, and melts at 68° . It is very unstable, and rapidly becomes brown on exposure to the air. Isoacetophorone yields two oximes, melting at 75° and 100° ; these have been described by Kerp (*loc. cit.*) and Tissier respectively. The former crystallises in the hexagonal system; $a:c=1:0.4676$. The latter forms triclinic crystals; $a:b:c=0.9930:1:0.6502$. $\alpha=115^\circ 36\frac{1}{2}'$, $\beta=101^\circ 56'$, $\gamma=98^\circ 26'$.

When isoacetophorone is suspended in water, and oxidised with potassium permanganate, it yields the monobasic acid, $C_9H_{14}O_4$, the ketonic acid, $C_8H_{14}O_3$, the lactone, $C_8H_{12}O_2$, and the dibasic acid, $C_6H_{10}O_4$.

The *acid*, $C_9H_{14}O_4$, is obtained by repeated distillation of the fraction of the oxidation product which boils at 195 — 210° under a pressure of 14 mm.; it melts at 99 — 100° . The acid separates alike from water and from a mixture of ether and light petroleum, in large, transparent, hemimorphic crystals belonging to the rhombic system; $a:b:c=0.6749:1:1.1016$. The *calcium* salt crystallises from water, and contains $2H_2O$.

The *ketonic acid*, $C_8H_{14}O_3$, is derived from the fraction which boils at 125 — 150° under a pressure of 14 mm.; the *calcium* salt crystallises from water and contains $1H_2O$. The *ethylic* salt boils at 104° under a pressure of 14 mm. The *oxime* dissolves readily in organic solvents excepting light petroleum.

The *lactone*, $C_8H_{12}O_2$, is obtained from the portion of the oxidation product which boils at 75 — 100° under a pressure of 14 mm. Treatment with boiling, concentrated alkali, regenerates the ketonic acid, from which it is derived by elimination of the elements of water.

The *acid*, $C_6H_{10}O_4$, crystallises from water, and melts at 139 — 140° . It is dibasic, and the *anhydride* boils at 104° under a pressure of 11 mm. The *anilic acid* (compare Abstr., 1897, i, 267) crystallises in lustrous leaflets; the *anil* crystallises from alcohol in prismatic needles, and melts at 85 — 86° .

Further oxidation of the ketonic acid, $C_8H_{14}O_3$, in alkaline solution with potassium permanganate gives rise to unsymmetrical dimethylsuccinic acid.

The authors represent the constitution of acetophorone (m. p. 28°)

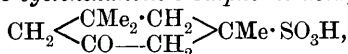
by the formula $\text{CO}(\text{CH}:\text{CMe}_2)_2$, isoacetophorone by the formula $\text{CMe}_2\text{CH}_2\text{COCH}_2\text{CMe}_2$, and camphorone by one or other of the expressions $\text{CMe}_2\text{C}(\text{CO}\cdot\text{CHMe})\text{CH}_2\text{CH}_2$ and $\text{CH}_2\text{CMeCH}(\text{CO}\cdot\text{CHMe})\text{CH}_2$.

M. O. F.

Camphorone, Isophorone, and Mesitylic Oxide. By WILHELM KERP and FRIEDRICH MÜLLER (*Annalen*, 1897, 299, 193—235. Compare Abstr., 1896, i, 447, and preceding abstract).—For reasons which are stated in the paper, the authors consider that isophorone is Δ^1 -trimethyl-1:3:3-cyclohexenone-5 (compare Knoevenagel and C. Fischer, Abstr., 1897, i, 611); they admit, however, that its behaviour on oxidation is more in agreement with the formula ascribed to it (isoacetophorone) by Brecht and Rübel. It is not improbable that the ketone is really a mixture of both isomerides. The view which is ultimately taken of the constitution of xylitone, $\text{C}_{12}\text{H}_{18}\text{O}$, the product of the condensation of acetone (1 mol.) with isophorone, must of course depend on the structure of the latter.

Isophorone boils at 98—100° under a pressure of 16 mm. The dibromide, $\text{C}_9\text{H}_{14}\text{Br}_2\text{O}$, is an unstable oil, which readily loses hydrogen bromide in the desiccator.

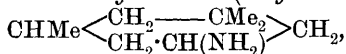
Trimethyl-1:3:3-cyclohexanone-5-sulphonic acid,



is obtained by the action of sulphurous acid on isophorone in aqueous suspension. The sodium salt separates from water and from alcohol in large crystals; the barium salt contains $2\text{H}_2\text{O}$.

Methylisobutylketosulphonic acid, $\text{SO}_3\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$, has been obtained from mesitylic oxide and sulphurous acid by Pinner (Abstr., 1882, 941), in the form of a sodium salt. The barium salt crystallises in lustrous leaflets containing $2\text{H}_2\text{O}$, and the silver salt is very sensitive to light and heat. Methylisobutylketoximesulphonic acid, $\text{NOH}\cdot\text{C}_6\text{H}_{11}\cdot\text{SO}_3\text{H}$, crystallises from absolute alcohol, and melts and decomposes at 185—190°. The sodium salt separates from alcohol in white needles and melts, evolving gas, at 218°; the barium salt crystallises from alcohol in leaflets, and contains $1\text{H}_2\text{O}$.

Trimethyl-1:3:3-amido-5-cyclohexane (dihydroisophorylamine),



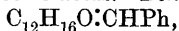
obtained from isophorone and ammonium formate, boils at 183—185°; the hydrochloride does not melt below 250°. The oxalate crystallises in white leaflets and melts at 221.5°; the carbamide melts at 125—125.5°.

Oxidation of isophorone with potassium permanganate yields unsymmetrical dimethylsuccinic acid, along with an acid, $\text{C}_8\text{H}_{12}\text{O}_4$, which crystallises from water in large, rhombic plates, and separates from benzene in stellate aggregates of prisms; it melts at 102—103°.

Metanitrobenzylideneisophorone, $\text{C}_9\text{H}_{12}\text{O}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is obtained by passing hydrogen chloride into a solution of metanitrobenzaldehyde in isophorone heated on the water bath; it crystallises from a mixture

of chloroform and light petroleum in small, sulphur-yellow needles and melts at 159—161°.

Xylitone, $C_{12}H_{18}O$, a viscous, yellowish oil, obtained as a by-product in the preparation of isophorone, boils at 120—122° under a pressure of 14 mm., and has the odour of geranium oil. The *oxime* boils at 162—164° under a pressure of 14 mm. The ketone is readily oxidised by potassium permanganate, which gives rise to acetic and unsymmetrical dimethylsuccinic acids. *Benzylidenexylitone*,



boils at 230—240° under a pressure of 14 mm.

Dihydrocamphoronesulphonic acid, $C_9H_{15}O \cdot SO_3H$, obtained by the action of sulphurous acid on camphorone, crystallises from a mixture of ether and alcohol, and dissolves very readily in water; the *barium* salt contains $2H_2O$.

β-Camphorone, $C_9H_{14}O$, is obtained by the action of alkalis on dihydrocamphoronesulphonic acid; it boils at 79—80° under a pressure of 14 mm. The *oxime* crystallises from alcohol and melts at 82—82·5°. A mixture of *β*-camphorone and benzaldehyde, when treated with alcoholic sodium ethoxide, yields a *compound* which boils at 200—205° under a pressure of 14 mm.

M. O. F.

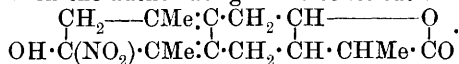
Bitter Almond Water. By PAUL FROMM (*Chem. Centr.*, 1897, i, 1101; from *Apoth. Zeit.*, 12, 254—257).—The so-called artificial bitter almond water contains hydrocyanic acid, benzaldehyde, benzaldehyde-cyanhydrin, water, and alcohol, whilst that obtained by distilling bitter almonds contains not only these compounds, but also small quantities of ammonia and of (amido?) substances which have a peculiar odour, and whose physiological action has not been investigated. The benzaldehyde-cyanhydrin does not distil over as such, but is formed in the distillate at first comparatively quickly, and then more slowly during about 8 days; after this time, however, combination ceases, although free benzaldehyde and free hydrocyanic acid are still present.

Analyses of samples of bitter almond water obtained from various firms are given, and show percentages of uncombined hydrogen cyanide varying from 6·41 to 17·64 of the total present. The author determines the quantity of benzaldehyde volumetrically by a modification of Denner's method of forming the hydrazone and then decomposing it with iodine (V. Meyer), which is said to give fairly concordant results, although those quoted are constantly 20 per cent. too low. In order to distinguish the artificial from the real product, advantage is taken of the fact that, whilst the latter is practically free from chlorine, the former contains small quantities derived from the commercial benzaldehyde used. Ten c.c. of the water are treated with 20 c.c. of hydrogen peroxide solution free from hydrochloric acid, and then warmed with 2—3 grams of pure sodium hydroxide until the bitter almond odour disappears; the residue obtained by evaporating and gently igniting is then tested with silver nitrate.

E. W. W.

Action of Nitric Acid on Desmotroposantonin. By AMERICO ANDREOCCHI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 309—313).—The production of desmotroposantonin by the action of hydrogen chloride or bromide on santonin may be explained on the assumption that the

halogen hydride first attaches itself to the ketonic group, and is then eliminated with formation of the hydroxy-compound. This view is supported by the formation of an additive compound of santonin and nitric acid; santonin is dissolved in nitric acid of sp. gr. = 1.40, and the solution allowed to evaporate spontaneously, or it is diluted with a little water, when large crystals separate of a compound to which the author assigns the constitution



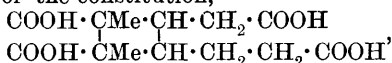
This nitrate decomposes at 120–140° with formation of some santonin, and is quantitatively dissociated into nitric acid and santonin by cold water.

Desmotroposantonin yields a *mononitro*-derivative of the constitution $\text{NO}_2\cdot\text{C}\cdot\text{CMe:C}\cdot\text{CH}_2\cdot\text{CH}\text{---}\text{O}$ with cooled dilute nitric acid;

$\text{OH}\cdot\text{C}\cdot\text{CMe:C}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CO}$, this crystallises in beautiful, yellow prisms, melting with decomposition at 191°, and gives a red *sodio*-derivative. On treatment with concentrated nitric acid at the ordinary temperature, desmotroposantonin yields a small proportion of a *nitroxy*-derivative which probably contains the group $\text{NO}_2\cdot\text{O}\cdot\text{C}\cdot\text{CMe:C}\text{---}$; it crystallises in

colourless prisms melting and decomposing at 240°, and is accompanied by a larger proportion of a substance which crystallises in yellow needles; the latter melts with decomposition at 145° and gives an orange-coloured *phenylhydrazone*.
W. J. P.

Oxidation Products of Santonic Acid. By LUIGI FRANCESCONI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 214–222).—Santonic acid, on oxidation with cold potassium permanganate (Abstr.,[†] 1894, i, 204), gives a tetracarboxylic acid, $\text{C}_{13}\text{H}_{18}\text{O}_8$ (α) which melts at 176°, being converted into the *monanhydride*, melting at 193°, of an isomeric acid (β). The α -acid has the specific rotation $[\alpha]_D = +28.56^\circ$, yields a liquid *tetramethylic* salt having $[\alpha]_D = +56.02^\circ$, and with acetic anhydride gives a *dianhydride* melting at 134°. The dianhydride takes up water yielding the α -acid, whilst the monanhydride combines with water to give the β -acid; the α -acid crystallises unaltered from boiling hydrochloric acid, but yields the β -acid when heated with hydrochloric acid at 180°. The β -acid, which is not altered by heating with hydrochloric acid at 180°, has the specific rotation $[\alpha]_D = +29.16^\circ$, and yields an inactive *tetramethylic* salt melting at 101°. Neither acid combines with hydroxylamine, phenylhydrazine, or bromine, nor decolorises permanganate. The author concludes that the α -acid is the *cis*-compound of the constitution,



whilst the β -acid is probably the *trans*-isomeride.

The α -acid, when heated with soda at 250–260°, gives hydrogen, carbonic anhydride, acetic acid, and a tribasic acid of the composition $\text{C}_{10}\text{H}_{10}\text{O}_6$, which is a mixture of a racemic inactive *acid* melting at 125° with a dextrorotatory *isomeride* of lower melting point. These

acids do not combine with hydroxylamine, phenylhydrazine, or bromine, and do not decolorise cold permanganate; the constitutions

$\text{COOH} \cdot \text{CHMe} \cdot \text{CH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH})_2$
and $\text{COOH} \cdot \text{CHMe} \cdot \text{CH}(\text{CH}_2 \cdot \text{COOH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ are assigned to the racemic and active acids respectively.

On heating the α -acid with soda at $380\text{--}400^\circ$, an oil of mint-like odour distills which consists of a ketone, $\text{C}_8\text{H}_{14}\text{O}$, boiling at $169\text{--}171^\circ$; as it is inactive, it is probably a *ketoethylhexamethylene* of the constitution, $\text{CHEt} \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \text{CO}$, derived from the racemic tribasic acid, $\text{C}_{10}\text{H}_{16}\text{O}_6$. On heating with red phosphorus and hydriodic acid, it yields a *hydrocarbon*, C_8H_{16} , of pleasant aromatic odour, boiling at 134° , which absorbs bromine with liberation of hydrogen bromide; it is probably an ethylhexamethylene.

The α -acid, $\text{C}_{13}\text{H}_{18}\text{O}_8$, is converted at $260\text{--}280^\circ$ into the *anhydride*, $\text{C}_{12}\text{H}_{14}\text{O}_4$, of a dibasic ketonic acid; the *acid*, $\text{C}_{12}\text{H}_{16}\text{O}_5$, melts at $213\text{--}216^\circ$ yielding the anhydride, and after crystallisation from water has the specific rotation $[\alpha]_D = -128.1^\circ$, whilst the crystals deposited from hydrochloric acid solution give the value $[\alpha]_D = -117.7^\circ$. The *dimethylic* salt melts at $92\text{--}93^\circ$; that prepared from methylic alcohol and hydrogen chloride has the specific rotation $[\alpha]_D = -106.6^\circ$, whilst a sample made from the silver salt and methylic iodide gave the value $[\alpha]_D = -111.4^\circ$. The *monomethylic* salt crystallises with $\frac{1}{2}\text{H}_2\text{O}$, and has the specific rotation $[\alpha]_D = -94.5^\circ$; it loses its water at 90° , and yields an *anhydride* melting at 135° on further heating. The *dimethylic* salt gives an *oxime* having the specific rotation $[\alpha]_D = +25.62^\circ$; the acid yields an *oxime* melting at 188° , and an *anhydride*, $\text{C}_{12}\text{H}_{14}\text{O}_4$, melting at 196° . Since the ketonic acid, $\text{C}_{12}\text{H}_{16}\text{O}_5$, is a derivative of the monanhydride of the β -tribasic acid, several constitutions are possible for it.

W. J. P.

Chrysotoxin. By C. JACOBY (*Chem. Centr.*, 1897, i, 483; from *Pharm. Centr. H.*, 38, 58).—Spasmodin or sphacelotoxin is not a homogeneous compound. Three substances, which possess similar therapeutic properties, were obtained from ergot, namely, *sphacelotoxin*, *secalintoxin* (a compound of sphacelotoxin with the inactive secalin), and *chrysotoxin* (a compound of sphacelotoxin with the inactive *ergochrysin*, $\text{C}_{21}\text{H}_{22}\text{O}_9$), identical with spasmodin. Chrysotoxin is pharmacologically as valuable as ergot, keeps unchanged for years, and in the form of its very soluble sodium compound is especially suitable for injecting. E. W. W.

Sphacelotoxin, the Active Principle of Ergot. By C. JACOBY (*Chem. Centr.*, 1897, i, 1059—1060; from *Arch. expt. Path. Pharm.*, 39, 85—143. Compare preceding abstract).—*Chrysotoxin*, $\text{C}_{21}\text{H}_{22}\text{O}_9$, which possesses the active properties of ergot of rye, is precipitated from the ethereal extract by light petroleum, and after repeatedly dissolving and precipitating, is obtained as a yellow, tasteless, and odourless powder. It crystallises in needles from a saturated solution in ether; it is easily soluble in most organic solvents, but is insoluble in light petroleum, water, and dilute acids. It is very slightly soluble in alkalis and ammonia, and since it is precipitated from such solutions by carbonic anhydride, its composition is probably more analogous to that

of a phenol than to that of an acid. These alkaline solutions undergo gradual decomposition, and after keeping some time are no longer precipitated by carbonic anhydride or acetic acid, but with hydrochloric acid yield a red precipitate of the inactive ergochrysinic acid.

Secalintoxin, $C_{13}H_{24}N_2O_2$, which has a physiological action similar to that of chrysotoxin but quite unlike that of Kobert's cornutin, is obtained from the ethereal extract by shaking it with acetic acid and precipitating the acid extract with sodium carbonate. It is very easily soluble in alcohol, ethylic acetate, benzene, and chloroform, slightly so in ether, very slightly in water, and insoluble in light petroleum. It is only slightly soluble in alkalis, and cannot be precipitated from such solutions, but dissolves easily in acids. The oxalate may be prepared by precipitating its ethereal solution with an alcoholic solution of oxalic acid.

Ergochrysin is obtained as an inactive, yellow substance by repeatedly dissolving chrysotoxin in glacial acetic acid and precipitating with water.

Secalin, $C_{29}H_{55}N_6O_{14}$, which is prepared by adding light petroleum to the ethereal solution of secalintoxin, is inactive, and crystallises in needles; it dissolves in a dilute solution of ammonia or sodium hydroxide. With alcohol and hydrochloric acid, it gives an intense violet coloration.

Chrysotoxin and secalintoxin owe their active properties to sphacelotoxin, which was obtained as a tar, and contains no nitrogen. It is converted into the inactive ergochrysin by the action of alkalis dissolved in alcohol. Sphacelotoxin probably occurs in these substances in a state of combination. E. W. W.

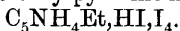
A New Reaction of, and a New Substance obtained from, Gambier Catechu. By KARL DIETERICH (*Chem. Centr.*, 1897, i, 245; from *Pharm. Centr.-H.*, 37, 855—860).—Two extracts of catechu are known in trade, the one, the real Pegu catechu, is obtained from the sapwood of *Acacia Catechu*, the other, Gambier catechu, obtained from *Uncaria Gambier*. The author finds that the latter furnishes the following characteristic reaction. When it is hydrolysed with a cold aqueous or alcoholic solution of potassium hydroxide and the alkaline solution shaken with light petroleum of sp. gr. = 0.7, the latter acquires a fine, green fluorescence; the substance dissolved can be obtained as a brittle, resinous mass which is insoluble in water and contains no nitrogen. A 2 per cent. solution of Gambier catechu in alcohol, when boiled for 10 minutes with dilute hydrochloric acid, gives a blood-red coloration; on the other hand, the red colour of solution of Pegu catechu almost entirely disappears on boiling with hydrochloric acid. Both kinds give green colorations with ferric chloride in alcoholic solution, but in the case of Pegu catechu the solution rapidly becomes brown, and gives a dark-brown precipitate which turns bluish-violet with alkalis. With ferrous salts, solutions of Gambier catechu give a green and Pegu catechu a grey coloration. When alcoholic potash solution is added to a dilute solution of Pegu catechu in alcohol, a violet precipitate is formed; Gambier catechu gives a yellowish-white precipitate. Gambier catechu is partially soluble in alcohol, and forms

a clear solution, whilst Pegu catechu is sparingly soluble and forms a turbid solution.

E. W. W.

Pyridine Periodides. By P. F. TROWBRIDGE (*Journ. Amer. Chem. Soc.*, 1897, 19, 322—331. Compare Abstr., 1896, 186, 316).—Pyridine methyl pentiodide, obtained when pyridine is added to an alcoholic solution of iodine containing methylic iodide, melts at 44·5°. *Pyridine methyl heptiodide* produced by the action of excess of iodine on pyridine methiodide in alcoholic solution, crystallises from dilute alcohol in slender, green needles melting at 26°; no higher periodide has been prepared.

Pyridine ethyl pentiodide forms black crystals melting at 83°, but as a compound of this nature should melt below 44°, the author thinks it probable that it may be ethylpyridine hydriodide tetriodide,



Pyridine hydriodide, $C_5NH_5, HI + H_2O$, forms white, needle-shaped crystals melting at 268° with some decomposition; if kept, it becomes brown and gives off pyridine. The *hydriodide*, C_5NH_5, HI , is made by adding freshly distilled hydriodic acid to well-cooled, pure pyridine; the white crystals, melting at 100°, can be recrystallised from water without taking up H_2O .

Pyridine hydrogen di-iodide prepared by treating pyridine with hydriodic acid containing iodine, or by adding an alcoholic solution of iodine to pure pyridine hydriodide, crystallises in dark brown needles melting at 188—191°; the *pentiodide* forms dark brownish-black crystals melting at 78—82°, and the *heptiodide* lustrous, green scales melting at 63—64°. The author has been unable to prepare the corresponding tri-iodide.

Pyridine ethyl tri-iodide forms bluish-black, thin, rhomboidal overlapping plates melting at 51°.

For the determination of the molecular weight of these substances, the freezing point method was employed, using phenol as solvent. The structure of these compounds is discussed, and the possibility of an iodine atom exerting an even valency is suggested.

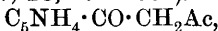
A. W. C.

Direct Introduction of Hydroxyl into 3-Hydroxypyridine. By RICHARD KUDERNATSCH (*Monatsh.*, 1897, 18, 613—628).—When 3-hydroxypyridine (20 grams) is fused with potassium hydroxide (250 grams), a *dihydroxypyridine*, $C_5NH_3(OH)_2$, is formed; to purify it, the crude product is converted into its acetyl compound, which is then hydrolysed by boiling water; on cooling, pure dihydroxypyridine crystallises out in colourless needles or white plates, which darken on exposure to the air. It is easily soluble in hot water, alcohol, and ethylic acetate, but almost insoluble in ether, benzene, chloroform, and petroleum. On being heated, it darkens at 220°, and melts and decomposes at 248° (uncorr.). Its solutions are coloured an intense blue by ferric chloride. The *hydrochloride*, $C_5H_5NO_2, HCl + H_2O$, crystallises in colourless plates, and melts at 106° (uncorr.), the anhydrous salt melting at 154° (uncorr.). The *platinochloride*,
 $(C_5H_5NO_2)_2, H_2PtCl_6 + H_2O$,
 crystallises in orange-red plates, and decomposes, without melting, at 130° (uncorr.); both these salts are easily decomposed by water. The

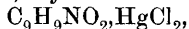
monacetyl derivative crystallises in colourless needles, melts at 156° (uncorr.), and is hydrolysed when boiled with water or alcohol.

It appears probable, from the mode of formation (compare Diamant, Abstr., 1896, i, 105), and from its failing to give condensation products with phthalic anhydride, or with orthophenylenediamine, that the new derivative is a 2:5-dihydroxypyridine. A *pyridoquinone* (*diketodihydroxypyridine*), $C_6H_5NO_2$, is obtained when it is oxidised with manganic hydroxide in sulphuric acid solution; this is insoluble in all ordinary solvents, but separates from fused acetanilide as a microcrystalline, brownish-violet powder. It decomposes above 200° without melting, and is reduced by sodium amalgam, and probably also by sulphurous acid, to the dihydroxy-compound from which it was prepared; it yields a crystalline compound with phenylhydrazine. W. A. D.

β -Acetoacetylpyridyl [3-Acetoacetylpyridine]. By ANDOR FERENCZY (*Monatsh.*, 1897, 18, 673—685).—3-Acetoacetylpyridine,



is prepared by adding an ethereal solution of ethylic nicotinate (1 mol.) and acetone (1 mol.) to sodium ethoxide, cooled so that the temperature does not rise above 40° ; it crystallises in soft, white needles, melts at 85° (uncorr.), and boils at 171° under a pressure of 15 mm. It is easily soluble in benzene, ether, alcohol, and acetone, but only sparingly so in water, and its aqueous and alcoholic solutions are coloured intensely red by ferric chloride. The *hydrochloride*, $C_6H_9NO_2 \cdot HCl$, crystallises in slender, slightly lustrous needles, and melts and decomposes at about 92° ; the *platinochloride*, $(C_6H_9NO_2)_2 \cdot H_2PtCl_6$, forms small, reddish-yellow, lustrous crystals, and melts, with decomposition, at 173 — 175° (uncorr.). Two compounds of the base with mercuric chloride are described; the first, $C_6H_9NO_2 \cdot HCl \cdot HgCl_2$, crystallises from dilute hydrochloric acid, and melts and decomposes at 123 — 125° (uncorr.); on dissolving this in alcohol, crystals of the second compound,

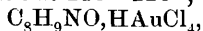


melting and decomposing at 107 — 110° (uncorr.), are obtained.

The *sodium* derivative, $C_6NH_4 \cdot CO \cdot CHNaAc$, of the diketone crystallises in slender, white needles. A *dioxime*, $C_9H_{11}N_3O_2$, is formed on adding hydroxylamine hydrochloride to 3-acetoacetylpyridine dissolved in dilute caustic soda; this crystallises from alcohol, is easily soluble in water, and melts at 79° (uncorr.); with phenylhydrazine, the diketone yields an oily compound, which is probably a pyrazole, analogous to that obtained in a similar manner from 2-acetoacetylpyridine (Micko, Abstr., 1897, i, 95); with ethylic iodide it yields an additive compound, which crystallises in light yellow plates and melts at 198 — 199° (uncorr.).

3-Acetoacetylpyridine is decomposed by alkalis into acetone and nicotinic acid, and, on reduction with zinc dust and acetic acid, yields a *keto-alcohol* (probably $C_6NH_4 \cdot CH(OH) \cdot CH_2Ac$), which melts at 115 — 117° . The *aurochloride*, $C_9H_{11}NO_2 \cdot HAuCl_4$ is a yellow, crystalline powder which melts at 143 — 145° .

By distilling 3-acetoacetylpyridine with zinc dust, the author obtained a colourless oil, which boiled at 210 — 220° ; its *aurochloride*,



crystallises in bright yellow needles. The paper closes with a comparison between the derivatives described, and the corresponding ones obtained by Micko (*loc. cit.*) from 2-acetoacetylpyridine. W. A. D.

Action of Ethylic Cyanacetate on Methyl Ethyl Ketone in Presence of Ammonia. By ERNESTO GRANDE (*Chem. Centr.*, 1897, i, 903; from *Atti R. Accad. Torino*, 32).—By treating methyl ethyl ketone with ethylic cyanacetate in presence of aqueous ammonia and evaporating, an *acid* is obtained which crystallises in leaflets and melts at 192—193°, and also its ammonium salt which does not melt at 260°; these compounds have not yet been completely examined. When ammonia is passed into a cooled mixture of the ketone and ethylic cyanacetate, hydrogen cyanide, ethane, and the ammonium salt of 3:5-dicyano-6-hydroxy-4-methyl- $\Delta^{3,6}$ -dihydropyridone or dicyano- γ -methylglutaconimide are formed. The last substance is identical with that obtained by Quenda and by Pasquali (see following abstracts). The magnesium salt crystallises with $4\frac{1}{2}\text{H}_2\text{O}$, and the copper salt with $9\text{H}_2\text{O}$. E. W. W.

Action of Ammonia and Ethylic Cyanacetate on Ethylic Ethylideneacetoacetate and Acetaldehyde. By ENRICO QUENDA (*Chem. Centr.*, 1897, i, 903; from *Atti R. Accad. Torino*, 32).—From the product of the action of ammonia and ethylic cyanacetate on ethylic ethylideneacetoacetate, a substance which melts at 210—212°, of unknown composition first separates, then the ammonium salt of dicyanomethylglutaconimide (see preceding abstract) and finally small quantities of ethylic dihydrocollidinedicarboxylate. The last owes its formation to Hantzsch's reaction between ammonia and the acetoacetate, whilst the glutaconimide results from the action of the cyanacetate and ammonia on the acetaldehyde which is formed by the decomposition of the acetoacetate, for if acetaldehyde be used instead of ethylic acetoacetate the same glutaconimide is produced. *Dicyanomethylglutaconimide*,
$$\begin{array}{c} \text{OH} \cdot \text{C} - \text{CH}(\text{CN}) \\ | \\ \text{N} \cdot \text{CO} \cdot \text{C}(\text{CN}) \end{array} \gg \text{CMe}$$
, crystallises in lustrous leaflets, is very easily soluble in water and alcohol, gives a violet-blue coloration with ferric chloride, and contains $2\frac{1}{2}\text{H}_2\text{O}$, which it retains at 244°; the anhydrous salt melts at 250—252°. The ammonium salt crystallises with $2\text{H}_2\text{O}$, and the barium salt with $4\text{H}_2\text{O}$. E. W. W.

Action of Ethylic Cyanacetate and Ammonia on Fatty Ketones. By ADALBERTO PASQUALI (*Chem. Centr.*, 1897, i, 903—904; from *Atti R. Accad. Torino*, 32).—By the action of ammonia and ethylic cyanacetate on acetone, according to Guareschi, diacetoneamine is first formed, and then a derivative of tetrahydropyridine,
$$\text{NH} \begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{C}(\text{CN}) \end{array} \gg \text{CMe}$$
. When higher homologues of acetone are used, different substances are obtained, according to whether the product is evaporated, or acidified with hydrochloric acid, but the ammonium salt of dicyanomethylglutaconimide (see preceding abstract) is invariably formed. This may result from the removal of a hydro-

carbon, RH, from an intermediate product, $\begin{matrix} \text{C}(\text{ONH}_4) \cdot \text{CH}(\text{CN}) \\ | \\ \text{N} \cdot \text{CO} \text{---} \text{CH}(\text{CN}) \end{matrix} \text{>CRMe}$,

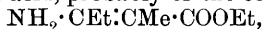
and in the case of methyl propyl ketone, the product of the reaction when treated with mercury was found to yield propane. By the action of ammonia and ethylic cyanacetate on methyl hexyl ketone, a compound, $\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}$, is formed, which crystallises in plates, melts at 152° , is slightly soluble in water and is decomposed into the ammonium salt of dicyanomethylglutaconimide and hydrogen cyanide by the action of aqueous ammonia; besides this, a substance, $\text{C}_3\text{H}_4\text{N}_2\text{O}$, which is slightly soluble in water, becomes brown at 300° without melting, and is not identical with cyanacetamide, is also produced. Methyl butyl ketone also yields the substance, $\text{C}_3\text{H}_4\text{N}_2\text{O}$, and a compound, $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2$, which melts at $177\text{--}178^\circ$, and when acted on by ammonia forms the ammonium salt of dicyanomethylglutaconimide. Methyl propyl ketone yields a compound, $\text{C}_8\text{H}_9\text{N}_3\text{O}$, which is also decomposed by ammonia with formation of the ammonium salt of dicyanomethylglutaconimide and hydrogen cyanide.

From acetone, a compound, $\text{C}_6\text{H}_5\text{N}_3\text{O}$, is obtained which crystallises in leaflets, melts at $213\text{--}214^\circ$, and is decomposed by ammonia, forming a substance, $\text{C}_3\text{H}_3\text{N}_4\text{O}_2$, which, however, does not yield dicyanomethylglutaconimide when treated with hydrochloric acid, but a compound which melts at $180\text{--}182^\circ$.

E. W. W.

Derivatives of Ethylic Propionylpropionate. By LUIGI SABATANI (*Chem. Centr.*, 1897, i, 904—905; from *Atti R. Accad. Torino*, 32.)—Ethylic propionylpropionate, obtained by the action of sodium on ethylic propionate, boils at 198° ; on agitating this liquid with aqueous ammonia, the ethylic salt of an amido-acid separates and propionylpropionamide remains in solution. By the action of ethylic cyanacetate on a solution of the latter, a clear liquid is obtained, which after a few days deposits a white precipitate of the ammonium salt of 3-cyano-6-hydroxy-4-ethyl-5-methyl- $\Delta^{3,6}$ -dihydropyridone or methylcyanethylglutaconimide, $\begin{matrix} \text{C}(\text{ONH}_4) \cdot \text{CHMe} \\ | \\ \text{N} \cdot \text{CO} \text{---} \text{C}(\text{CN}) \end{matrix} \text{>CEt}$; this, on exposure to the air, becomes red. It dissolves in 381 parts of water, reddens blue litmus, decomposes carbonates, gives a blue coloration with ferric chloride and a red precipitate with copper sulphate, does not react with nitrites or with bromine, turns brown at 250° , and melts and decomposes at $261\text{--}262^\circ$. The ammonium, silver, sodium, barium, and copper salts were prepared and analysed.

On shaking ethylic propionylpropionate with methylamine, the ethylic salt of an amido-acid, probably of the composition



separates and propionylpropionomethylamide, $\text{COEt} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NHMe}$, remains in solution. By the action of ethylic cyanacetate on the latter, a methylamine salt is obtained from which hydrochloric acid liberates 3-cyano-6-hydroxy-1:3-dimethyl-4-ethyl- $\Delta^{3,5}$ -dihydropyridone or methylcyanethylglutaconmethylimide, $\text{NMe} < \begin{matrix} \text{C}(\text{OH}) : \text{CMe} \\ \text{CO} \text{---} \text{C}(\text{CN}) \end{matrix} \text{>CEt}$; this is a monobasic acid, slightly soluble in water. It melts and decomposes at 198° , gives a blue coloration and a white precipitate with ferric chloride, a

white precipitate with bromine, a yellow coloration when warmed with sodium nitrite, and is precipitated by silver nitrate but not by copper salts.
E. W. W.

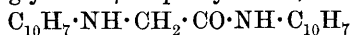
Synthesis of Pyridine Compounds and Hantzsch's Reaction. By ICILIO GUARESCHI (*Chem. Centr.*, 1897, i, 927—928; from *Atti R. Accad. Torino*, 32. Compare Abstr., 1897, i, 168—169).—In the reaction investigated by Quenda (see preceding abstracts), dicyanomethylglutaconimide is formed by the condensation of acetaldehyde (1 mol.), ethylic cyanacetate (2 mols.), and ammonia (1 mol.), with elimination of alcohol, water, and hydrogen. It has not yet been ascertained whether the hydrogen is liberated or takes part in secondary reactions. The formation of the substance which melts at 210—212° may be due to a similar reaction between ethylic acetoacetate, acetaldehyde and ammonia, in molecular proportion. Benzaldehyde, ethylic cyanacetate, ethylic acetoacetate, and ammonia react to form a compound which melts at 222—223°, and which may also result from a like reaction between these compounds in molecular proportion. The author proposes to ascertain whether, by a further extension of Hantzsch's reaction, aldehyde-ammonia, aldehyde, and ethylic cyanacetate may not form a substance of the formula $N \begin{smallmatrix} \text{CH} - \text{CH}_2 \\ \text{CO} \cdot \text{C}(\text{CN}) \end{smallmatrix} \text{CMe}$. From the fact that, by the action of ethylic cyanacetate on ketones of the type $R \cdot \text{CO} \cdot \text{Me}$ in presence of ammonia (see Pasquali, preceding abstracts), dicyanomethylglutaconimide and a hydrocarbon are always formed, it is evident that the group COMe is eliminated, the residue forming a hydrocarbon. Intermediate products are obtained which, when decomposed by water, yield dicyanomethylglutaconimide and a hydrocarbon.
E. W. W.

Alkoxides of 3-Hydroxyquinoline. By ADOLPH CLAUS and HANS HOWITZ (*J. pr. Chem.*, 1897, [ii], 56, 438—444. Compare Abstr., 1896, i, 698).—3-Methoxyquinoline methiodide, already prepared by Skraup, can be obtained quite well from 3-hydroxyquinoline (1 mol.) by heating it with methylic iodide (rather more than 2 mols.) and potassium hydroxide (1 mol.); it melts and decomposes at 235—240°, and crystallises with $1\text{H}_2\text{O}$, as well as anhydrous. Treatment with silver chloride converts it into the *methochloride*, which decomposes at 234°, and crystallises with $1\text{H}_2\text{O}$. Both these salts, when heated with potash, yield a product which dissolves in ether forming a yellow solution, and remains, after evaporation of the ether, as an unstable, viscid liquid; this is probably a methylenequinolinium base (Abstr., 1892, 878). With silver oxide and water, they yield 3-methylquinolinium methohydroxide, which is insoluble in ether, and forms yellowish-red, unstable crystals; acids convert it into the corresponding metho-salts.

3-Ethoxyquinoline methiodide is obtained from 3-ethoxyquinoline and methylic iodide at 100°; it is yellow, decomposes at 195—197°, and crystallises with $1\text{H}_2\text{O}$. Treatment with silver chloride converts it into the *methochloride*, which decomposes above 200°, and crystallises with $1\text{H}_2\text{O}$. The *ethobromide* is obtained by using ethylic bromide, at 100°; it crystallises with $2\text{H}_2\text{O}$, and then melts at about 100°; when anhydrous, it decomposes at 210°. The *benzylochloride*, obtained with

benzylic chloride at 200° crystallises with $3\text{H}_2\text{O}$, and then melts at 96° ; this, when heated with silver oxide and water, yields *both* the benzylidene and the benzylhydroxide base.
C. F. B.

Synthesis of Naphthindole Derivatives. By OSCAR HINSBERG and A. SIMCOFF (*Ber.*, 1898, 31, 250—254).—A small quantity of Cosiner's β -naphthylglycocine- β -naphthylamide,



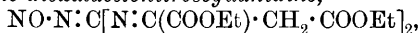
(Abstr., 1887, 605), is obtained when sodium naphthindolesulphonate is boiled with an excess of moderately dilute potassium hydroxide. If the sodium salt is distilled by itself, or, still better, with twice its weight of zinc dust in a stream of dry hydrogen at as low a temperature as possible, the chief product is β -naphthindole, $\text{C}_{10}\text{H}_6\left<\begin{smallmatrix}\text{NH} \\ \text{CH}\end{smallmatrix}\right>\text{CH}$, a considerable amount of an oily product being also formed. The indole forms large crystals melting at $39\text{--}40^{\circ}$ and is readily soluble in most organic solvents. It yields a brownish-red, crystalline *picrate*, and with sodium nitrite and hydrochloric acid gives a brown precipitate. It is not identical with Schlieper's β -naphthindole (Abstr., 1887, 153). Isonitrosonaphthoxindole, which has been previously obtained by converting naphthindolesulphonic acid into naphthoxindole and then nitrosating, is more readily obtained as follows. A solution of potassium naphthindolesulphonate (1 gram) in 100 c.c. of hot water is cooled to 70° and then treated with acetic acid (10 c.c.) and a 10 per cent. solution of sodium nitrite (10 c.c.); the brownish-red precipitate of crude isonitrosonaphthoxindole, after being purified by recrystallisation from water, melts at about 230° . β -Naphthisatin is best obtained by boiling the isonitroso-compound (1 gram) with 20—30 c.c. of sulphuric acid (b. p. 130°) for $2\frac{1}{2}$ —3 hours. After recrystallisation from alcohol, it melts at 252° .

Naphthindophenazine, $\text{C}_{10}\text{H}_6\left<\begin{smallmatrix}\text{NH}\cdot\text{C}:\text{N} \\ \text{C}:\text{N}\end{smallmatrix}\right>\text{C}_6\text{H}_4$, is formed when ortho-phenylenediamine and β -naphthisatin are heated at 250° in an oil bath. The crude product is finely powdered, washed with water and alcohol, and then recrystallised from acetic acid; it forms pale yellow needles which melt above 300° and gives a deep violet coloration with sulphuric acid.

When β -naphthisatin is reduced with acetic acid and zinc dust, it yields β -naphthodioxindole, $\text{C}_{10}\text{H}_6\left<\begin{smallmatrix}\text{NH} \\ \text{CH}(\text{OH})\end{smallmatrix}\right>\text{CO}$, which is precipitated when the hot acetic acid solution is poured into water. After recrystallisation from alcohol containing a small quantity of sulphurous anhydride in solution, it is obtained in the form of colourless, or slightly brown, crystals melting at 216° . It is readily oxidised by atmospheric oxygen to β -naphthisatin.
J. J. S.

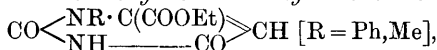
Action of Ethylic Oxalacetate on Guanidine and Derivatives of Carbamide. By R. MÜLLER (*J. pr. Chem.*, 1897, [ii], 56, 475—506. Compare Abstr., 1897, i, 549, where *for* ethylic oxalate, dioxalguanidine, and dioxalcarbamide *read* ethylic oxalacetate, dioxal-

acetoguanidine, and dioxalacetocarbamide).—These substances are obtained by mixing ethylic oxalacetate with guanidine carbonate or carbamide, and a little acetic acid, heating the mixture to boiling, and then allowing it to remain for several days until crystallisation is complete. Ethylic dioxalacetoguanidine is decomposed by cold dilute hydrochloric acid into ethylic oxalacetate and guanidine; ethylic dioxalacetocarbamide is much more stable, and is not decomposed, even on boiling; alcoholic hydrochloric acid at 110° decomposes it completely, eliminating carbonic anhydride and ammonia. When nitrous anhydride is passed into a cooled solution of ethylic dioxalacetoguanidine, *ethylic dioxalacetoneitrosoguanidine*,



melting and decomposing at 127–128°, is formed; ethylic dioxalacetocarbamide yields, first carbamide nitrate, and eventually ammonium nitrate. With neither ethylic dioxalacetoguanidine nor ethylic dioxalacetocarbamide does either ammonia, aniline, or sodium ethoxide yield any well-defined product; fuming nitric acid does act on them, however, yielding products that melt at 98·5° and 131° respectively.

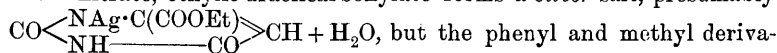
Ethylic phenyluracilcarboxylate and methyluracilcarboxylate,



are obtained in the same manner as the unsubstituted uracilcarboxylate, starting from phenyl- and methyl-carbamide; they melt at 185° and 139·5° respectively. Ethylic uracilcarboxylate yields a

monacetyl derivative, $\text{CO} \begin{array}{c} \text{NAc}\cdot\text{C}(\text{COOEt}) \\ \text{NH} \text{-----} \text{CO} \end{array} \text{CH}$, melting at 139°; the

phenyl- and methyl-uracilcarboxylates yield no such derivatives. With silver nitrate, ethylic uracilcarboxylate forms a *silver* salt, presumably



but the phenyl and methyl derivatives form no such salts; this salt reacts with methylic iodide, but the product, curiously enough, melts at 112°, lower by 27° than the ethylic methyluracilcarboxylate described above. With alcoholic sodium ethoxide at the ordinary temperature, ethylic uracilcarboxylate forms

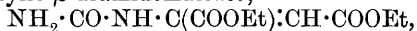
a *disodium* salt, probably $\text{CO} \begin{array}{c} \text{NH}\cdot\text{C}(\text{COONa}) \\ \text{NNa} \text{-----} \text{CO} \end{array} \text{CH}$, and this, with

silver nitrate, yields the corresponding *disilver* salt; ethylic phenyl- and methyl-uracilcarboxylates, on the other hand, appear to yield products of the composition $\text{CO} \begin{array}{c} \text{NR}\cdot\text{C}(\text{COOEt}) \\ \text{NNa} \text{-----} \text{CO} \end{array} \text{CNa}$. These products

are decomposed by cold dilute hydrochloric acid, *β-phenyluramidacrylic acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, melting and decomposing at 272°, and *β-methyluramidacrylic acid*, which is still unmelted at 300°, being formed. Ethylic uracilcarboxylate, in acetic acid solution, reacts with nitrous anhydride, yielding a product, $\text{C}_9\text{H}_8\text{N}_6\text{O}_8$, that melts at 240°, and forms compounds $\text{C}_9\text{H}_6\text{Ag}_2\text{N}_6\text{O}_8$ and $\text{C}_7\text{Na}_4\text{N}_6\text{O}_8$ when treated with silver nitrate and alcoholic sodium ethoxide respectively; with cold, red, fuming nitric acid, it yields the same product. It does not react with benzaldehyde, and therefore cannot contain a methylene group.

Neither triphenylguanidine nor diphenylcarbamide will condense

with ethylic oxalacetate; this makes it probable that in the condensation the water is eliminated from $\cdot\text{NH}_2$ and $\cdot\text{CO}\cdot$ groups of the carbamide and oxalacetate respectively, and not from $\cdot\text{NH}_2(\cdot\text{NHR})$ and $\cdot\text{C}(\text{OH})\cdot$ (tautomeric form of the oxalacetate). In the condensation of carbamide with ethylic oxalacetate to ethylic uracilcarboxylate, the formation of ethylic β -uramidomaleate,



as an intermediate product must be assumed.

C. F. B.

Reduction of 2:4-Pyrrodiazoles. By AMERICO ANDREOCCHI and NICOLA CASTORO (*Real. Accad. Linc.*, 1896, [v], 5, ii, 343—346).—On

reducing 1-phenyl-2:4-pyrrodiazole, $\begin{smallmatrix} \text{CH:N} \\ \text{N:CH} \end{smallmatrix} > \text{NPh}$, in absolute alcohol

with sodium, aniline, methylamine, ammonia, a little hydrogen cyanide, and a small proportion of a pyrrodiazoline are produced. The investigation is being continued.

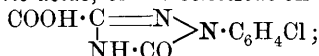
W. J. P.

Action of the Phosphorus Chlorides on Oxygenated Derivatives of 2:4-Pyrrodiazoles. By AMERICO ANDREOCCHI (*Real. Accad. Linc.*, 1897, [v], 6, i, 114—120 and 217—235).—1-Phenyl-3-methyl-

pyrrodiazolone, $\begin{smallmatrix} \text{CMe:N} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{NPh}$, is converted by phosphorus penta-

chloride at 150° into a mixture of two isomeric *monochloro*-derivatives, $\text{C}_9\text{H}_8\text{N}_3\text{OCl}$, which crystallise, one in thin needles melting at 247° , and the other in prisms melting at 163° ; at lower temperatures, phosphoric anhydride, or a mixture of phosphorus trichloride, and pentachloride, converts the diazolone into a condensation product, $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}$, which crystallises in large prisms melting at 140° . A similar *anhydride*, $\text{C}_{16}\text{H}_{12}\text{N}_6\text{O}$, is obtained by treating 1-phenyl-5-pyrrodiazolone with phosphoric anhydride or a mixture of the two chlorides; it crystallises in needles melting at 162° , and both anhydrides are insoluble in alkalis; the two isomeric chloro-derivatives melting at 247° and 163° are *chlorophenyl-methylpyrrodiazolones* of the constitution $\begin{smallmatrix} \text{CMe:N} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, and

when oxidised with alkaline permanganate yield isomeric *chlorophenylpyrrodiazolonecarboxylic acids*, of the constitution



that from the substance melting at 247° melts at 130 — 200° , and decomposes, yielding a *substance* melting at 257° , whilst the acid from the compound melting at 163° melts and decomposes at 150 — 155° , yielding a *substance* melting at 152° . These products are *chlorophenylpyrrodiazolones* of the constitution $\begin{smallmatrix} \text{CH=N} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, and the isomeride

melting at 257° is also obtained by treating the phenylpyrrodiazolone with phosphorus pentachloride.

1-Phenyl-5-pyrrodiazolone, when treated with a mixture of phosphorus pentachloride and oxychloride, yields the following compounds, namely, 1-chlorophenyl-5-chloropyrrodiazole, $\begin{smallmatrix} \text{C:HN} \\ \text{N:CCl} \end{smallmatrix} > \text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, which

crystallises in laminae melting at 70° ; 1-phenyl-5-chloropyrroldiazole, which crystallises in large prisms melting at 54° ; and 1-phenylpyrroldiazole, $\begin{matrix} \text{CH:N} \\ \text{N:CH} \end{matrix} > \text{NPh}$, which melts at 47° and boils at 266° ; this is also obtained by the action of phosphorus pentasulphide on 1-phenyl-5-pyrroldiazolone, or on 1-phenyl-3-oxypyrroldiazole. A compound which crystallises in thin, transparent laminae melting at 133° , and seems to have the composition of a chlorophenylpyrroldiazole and an anhydride of the composition $\text{C}_{16}\text{H}_{11}\text{ClN}_6\text{O}$, which crystallises in thin needles, are also obtained.

The following compounds have been prepared in like manner from 1-phenyl-3-methylpyrroldiazolone. 1-Chlorophenyl-3-methyl-5-pyrroldiazole, $\begin{matrix} \text{CMe:N} \\ \text{N=CCl} \end{matrix} > \text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, which crystallises in long, transparent needles melting at 95° ; 1-phenyl-3-methyl-5-pyrroldiazole, which crystallises in large prisms melting at 84° , and a substance which crystallises in long needles melting at 123° and has the composition of a 1-chlorophenyl-3-methylpyrroldiazole. A brown, viscous residue not volatile with steam is also obtained.

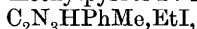
The action of a mixture of phosphorus pentoxide and oxychloride on phenylurazole yields a phenyldichloropyrroldiazole, which crystallises in small prisms melting at 94° , and probably has the constitution $\begin{matrix} \text{CCl:N} \\ \text{N:CCl} \end{matrix} > \text{NPh}$.

Phenylpyrroldiazolone, when heated with phosphorus oxychloride in a closed tube at 180° , yields the 1-phenyl-5-chloropyrroldiazole melting at 54° , and an anhydride of the composition $\text{C}_{16}\text{H}_{12}\text{N}_6\text{O}$, which melts at 162° . The same two substances and the 1-phenylpyrroldiazole melting at 47° are obtained by heating the phenylpyrroldiazolone with phosphorus trichloride in a closed tube at 180° .

The 1-phenyl-3-oxypyrroldiazole, when heated with phosphorus oxychloride at 200° yields 1-phenyl-3-chloropyrroldiazole, $\text{C}_2\text{N}_3\text{PhHCl}$, which melts at 76° and boils at 299° .

W. J. P.

1-Phenyl-3-methylpyrrol-2:4-diazole Ethiodide and Ethobromide. By AMERICO ANDREOCCHI (*Real. Accad. Linc.*, 1897, [v], 6, i, 293—295).—1-Phenyl-3-methylpyrrol-2:4-diazole ethiodide,



prepared by heating the diazole with ethylic iodide at 100 — 120° for several hours, crystallises in hard prisms melting at 181 — 182° , and is very soluble in water. The corresponding ethobromide crystallises in large prisms melting at 222 — 224° , and is also very soluble in water.

W. J. P.

Constitution of the Pyrroldiazolones. By AMERICO ANDREOCCHI (*Real. Accad. Linc.*, 1897, [v], 6, i, 378—386).—This paper is of theoretical importance only, and contains no new experimental results.

W. J. P.

Caffeine Compound in Kola. By JAMES W. T. KNOX and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1897, 19, 63—90).—When kola seed is cut or bruised, chemical action at once takes place,

as is seen by the change in colour from pink to reddish-brown; that this is due to the action of a diastatic ferment seems probable, for no colour is developed when the freshly-cut seed is placed in boiling water. Cold does not impair the potency of the ferment, but seems to preserve it.

The method of Dohme and Engelhardt (*Amer. Drugg.*, 1896, 12) for the assay of kola only gives about one-half of the total caffeine, and the authors recommend the following process. To the measured caffeine solution acidified with hydrochloric acid, a definite volume of Wagner's reagent is added in excess, and after allowing the precipitate to settle, the liquid is filtered through asbestos. The excess of iodine is then titrated with decinormal thiosulphate solution, and from this the amount of Wagner's solution used up can be calculated, 1 c.c. corresponding with 0.00485 gram of anhydrous caffeine.

Hydrolysis with dilute acids is unsuitable for the complete recovery of the alkaloids of kola from their natural combination (kolanin), but if freshly precipitated lead hydroxide is used, the whole of the caffeine is liberated; this affords a trustworthy method for the determination of the combined alkaloids in kola. This action of kolanin with lead hydroxide indicates that it is of a tannin-like character, for there is reason to believe that the glucose obtained by the decomposition of the so-called glucoside (kolanin) with mineral acids exists primarily in combination with a tannin-like substance; the liberation of glucose is, therefore, not necessarily simultaneous with that of caffeine or a consequence of it. In all probability, kolanin is a combination of caffeine and theobromine with a glucoside-tannin. When an aqueous infusion of kola is poured into a 10 per cent. solution of caffeine acidified with hydrochloric acid, a precipitate is formed, and this "caffeine kolatannate" is identical in appearance and properties with kolanin, and differs but slightly from it in composition.

When kolanin is treated with diastase at 50—53°, caffeine is precipitated, but from a control experiment it appears that precipitation is due rather to the effect of water and heat than to the diastase, and the liberation of caffeine by the kola ferment itself is to be attributed to the same cause, for if the kola be sterilised, thus checking the formation of the coloured compound (kola red), the amount of alkaloid liberated is not diminished; caffeine and kola red are not therefore joint products of the one hydrolysis of a glucoside, as concluded by previous investigators.

A slight modification of Kunze's method (*Abstr.*, 1894, ii, 168) for the estimation of theobromine in presence of caffeine gave very satisfactory results.

The melting point of the mixed free alkaloids and of the combined alkaloids of kola is the same, 225—227°, corresponding fairly well with that of pure caffeine.

The free tannin of kola is a light red to red-brown substance having a faintly acid and astringent taste and behaving like other tannins with iron salts, gelatin, and alkaloids. It is a glucosidal compound, as on hydrolysis with dilute mineral acids it yields glucose and a dark brown substance insoluble in water and alcohol. The combined tannin agrees with the above in appearance and properties.

A. W. C.

New Synthesis of Adenine and its Methyl Derivatives. By EMIL FISCHER (*Ber.*, 1898, 31, 104—122. Compare this vol., i, 48).—2-Chloro-6-amido-8-oxypurine is converted by phosphorus oxychloride into a mass which contains a large amount of dichloro-adenine, although this substance has not been isolated from it. When the crude product is warmed with hydriodic acid, it readily yields adenine, identical in all respects with the natural product and with that previously obtained from trichloropurine.

Synthesis of the Methyladenines.—2:6-Dichloro-8-oxy-9-methylpurine is converted by alcoholic ammonia at 140—150° into 2-chloro-6-amido-8-oxy-9-methylpurine, $\begin{array}{c} \text{N:C(NH}_2\text{)} \cdot \text{C} \cdot \text{NH} \\ | \quad | \\ \text{CCl:N} \text{---} \text{C} \cdot \text{NMe} \end{array} \text{>CO}$, which crystallises in

short, lustrous needles, decomposes above 360°, and yields crystalline salts with hydrochloric, nitric, and sulphuric acids. When this base is heated with phosphorus oxychloride, 2:8-dichloro-6-amido-9-methylpurine, $\begin{array}{c} \text{N:C(NH}_2\text{)} \cdot \text{C} \text{---} \text{N} \\ | \quad | \\ \text{CCl:N} \text{---} \text{C} \text{NMe} \end{array} \text{>CCl}$, is formed, which crystallises in rhombo-

hedral forms, melts at 270° (corr.), and yields crystalline salts with mineral acids. On reduction with hydriodic acid, it yields the 9-methyladenine melting at 308—310° (corr.), which has been previously described. The isomeric 7-methyladenine is obtained by a similar series of operations from 2:6-dichloro-8-oxy-7-methylpurine. 2-Chloro-6-amido-8-oxy-7-methylpurine crystallises with 1H₂O in elongated, lustrous plates, which decompose when heated, and are very sparingly soluble in water. The base yields salts both with acids and bases, the sodium salt crystallising in slender, flexible needles. 2:8-Dichloro-6-amido-7-methylpurine crystallises in long, slender, flexible needles, and, when heated, decomposes without melting. It is sparingly soluble in water, and readily yields salts with acids but not with bases. 7-Methyladenine, $\begin{array}{c} \text{N:C(NH}_2\text{)} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{CH:N} \text{---} \text{C} \text{---} \text{N} \end{array} \text{>CH}$, forms a neutral

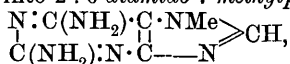
solution in water, from which it separates as a granular powder, melting at 351° (corr.), and partially subliming at a higher temperature. The hydrochloride crystallises in microscopic, rectangular tablets, the nitrate in fascicular groups of needles, and the sulphate in well-developed prisms. This new base can also be obtained from 2:6-dichloro-7-methylpurine, which is converted by ammonia into 2-chloro-6-amido-7-methylpurine, a compound which crystallises in slender needles, and melts at about 284° (corr.), evolving gas. When heated with fuming hydrochloric acid, this substance yields heteroxanthine, whilst with hydriodic acid, 7-methyladenine is formed.

The Methylhypoxanthines.—By the action of nitrous acid, the methyladenines are converted into the corresponding methylhypoxanthines, of which the 7-methyl derivative has already been described. 9-Methyl-

hypoxanthine, $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{C} \text{---} \text{N} \\ | \quad | \\ \text{CH:N} \text{---} \text{C} \cdot \text{NMe} \end{array} \text{>CH}$, which is only sparingly soluble

in water, crystallises in narrow plates, and melts and decomposes at about 390° (corr.). It yields salts both with acids and bases, and on methylation is converted into a crystalline product which is probably a dimethyl-compound, but has not been analysed. 2-Chloro-6-amido-

8-oxy-7-methylpurine is converted by hydrochloric acid at 130° into 6-amido-2 : 8-dioxy-7-methylpurine, $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NMe} \\ | \quad | \\ \text{CO}\cdot\text{NH}-\text{C}-\text{NH} \end{array} > \text{CO}$, which crystallises with $1\text{H}_2\text{O}$ in microscopic plates, is very sparingly soluble in water, and decomposes above 320° . It gives the murexide reaction, but does not yield guanidine on oxidation with hydrochloric acid and sodium chlorate. The hydrochloride crystallises in prisms or slender needles, the sulphate in spherical aggregates, and the sodium salt in very slender, flexible needles. Dichloro-7-methylpurine is converted by aqueous ammonia into 2 : 6-diamido-7-methylpurine,



crystallising in long, slender needles, which melt and decompose at about 390° (corr.).

2-Chloro-6-methylamido-7-methylpurine, obtained by the action of methylamine on the dichlorinated base, crystallises with $2\text{H}_2\text{O}$ in lustrous plates, melts at 269° (corr.), and decomposes at a higher temperature. The hydrochloride, nitrate, sulphate, aurochloride and platinochloride are all crystalline, the last-named being only very sparingly soluble in water. Hydrazine acts on the dichloro-base in a somewhat similar manner to methylamine, but also forms complicated products. Chloro-7-methylhydrazidopurine, $\text{C}_6\text{H}_4\text{N}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}_2$, crystallises in bundles of slender needles, and decomposes when heated. The base readily reduces platonic chloride and Fehling's solution, its constitution as a primary hydrazine being thus established. The salts with acids are all crystalline, the sparingly soluble picrate melting at $160-162^{\circ}$. Hydrazomethylchloropurine, $\text{C}_6\text{H}_4\text{N}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{N}_4\text{Cl}$, which is formed along with the foregoing compound, crystallises with $1\text{H}_2\text{O}$, and decomposes very readily when heated. It dissolves in both bases and acids, forming crystalline salts with the latter. A. H.

A Product of Hydrolysis from Arginine. By ERNST SCHULZE and ERNST WINTERSTEIN (*Ber.*, 1897, 30, 2879—2882).—It has been already shown by Schulze and Likiernik (*Abstr.*, 1891, 1521) that carbamide is produced by the hydrolysis of arginine with baryta. The authors have identified the remaining product as ornithin, described by Jaffé (*Abstr.*, 1878, 584). Regarding this substance as diamido-valeric acid, they ascribe to arginine the constitution



M. O. F. —

Non-nitrogenous Decomposition Products of Morphine. By EDUARD VONGERICHTEN (*Ber.*, 1898, 31, 51—56. Compare this vol., i, 98).—Acetylmethylmorpholquinone, $\text{C}_{17}\text{H}_{12}\text{O}_5$, is obtained by oxidising acetylmethylmorphol in glacial acetic acid solution with chromic acid; it crystallises from glacial acetic acid in lustrous, yellow needles, and melts at $205-207^{\circ}$. The solution in concentrated sulphuric acid is bluish-red, and a greenish-blue liquid is formed on treating the quinone with sodium hydroxide dissolved in methylic alcohol. It undergoes Laubenheimer's condensation when treated with toluene and glacial acetic and sulphuric acids. The production

of the quinone is analogous to the formation of acetylthebaolquinone (Freund, Abstr., 1897, i, 497). The *azine*, $C_{24}H_{18}N_2O_3$, is obtained from the quinone and orthotolylenediamine, and melts at 212° ; the solution in concentrated sulphuric acid is deep greenish-blue, becoming bluish-red on dilution.

Attempts to improve the method of preparing morphenol methylic ether have led to the observation that this compound is derived from the methohydroxide of β -methylmorphimethine rather than from the α -derivative.

Oxidation of acetylmorphenol (m. p. 140°) yields an orthodiketone having phenolic properties; the compound is a derivative of phenanthraquinone.

M. O. F.

Euquinine. By CARL VON NOORDEN (*Chem. Centr.*, 1897, i, 182, from *Centr. f. inn. Med.*, 17, 1225).—*Euquinine* (quinine ethylic carbonate, $C_{20}H_{23}N_2O \cdot O \cdot COOEt$), is obtained by the action of ethylic chlorocarbonate on quinine. It crystallises in white needles, melting at 95° , has an alkaline reaction, is nearly tasteless, and forms crystallisable salts with acids. Like quinine, it shows a strong blue fluorescence when dissolved in sulphuric or nitric acid. It is recommended as a medicament in place of quinine, 1.5 to 2 grams of euquinine being equivalent to 1 gram of quinine salts.

W. D. H.

Derivatives of Tropine. By A. VAN SON (*Arch. Pharm.*, 1897, 235, 685—693).—*Tropinebetaine chloride*, $C_8H_{15}ONCl \cdot CH_2 \cdot COOH$, is obtained by heating together tropine and monochloroacetic acid; it forms an *aurochloride* crystallising from hot water in beautiful, feathery needles containing $1H_2O$ and melting at 223 — 224° , and a *platinochloride* separating from water in groups of prismatic crystals containing $2H_2O$ and melting at 227° . *Tropinecholine chloride*, prepared by the interaction of ethylenechlorhydrin and tropine, forms an *aurochloride* crystallising in long needles melting at 216° , and a *platinochloride* melting at 216 — 217° . *Tropinethylene bromide*, obtained from tropine and ethylenic dibromide, crystallises from alcohol in plates melting at 205 — 206° ; when treated with silver chloride, one bromine atom is replaced by chlorine, and the resulting chlorobromide gives an *aurochloride* crystallising in plates and melting at 206 — 207° , and a *platinochloride* crystallising in yellowish-red plates or needles and melting at 215° . When the ethylenic bromide compound is treated with silver nitrate, it is converted into tropinecholine nitrate, as proved by the preparation of the *aurochloride*.

Tropineneurine, $C_8H_{15}ON(OH) \cdot CH:CH_2$, results from the action of freshly precipitated silver oxide on tropinethylene bromide. The *neurochloride* forms feathery needles melting at 223° , and the *platinochloride* crystallises in plates melting and slightly decomposing at 214° . On treatment with hydrogen bromide, it is converted into *tropine-neurine bromide*, $C_8H_{15}ONBr \cdot CH:CH_2$, crystallising from alcohol in colourless needles, which blacken at 215° without melting. When treated with bromine in alcoholic solution, a *tribromide* is formed crystallising in colourless needles which decompose at 240° without melting. The *aurochloride* forms small needles melting at 214 — 215° .

A. W. C.

Crystalline Physostigmine [Eserine]. By N. A. ORLOFF (*Chem. Centr.*, 1897, i, 1214; from *Pharm. Zeit. Russ.*, 36, 213—214).—By precipitating an aqueous solution of eserine sulphate with ammonia, allowing the precipitate to remain in the liquid for some time, and occasionally shaking, the alkaloid is obtained in a crystalline form. The author recommends the above as a general method of preparing crystalline alkaloids. E. W. W.

Pilocarpidine. By C. EMANUEL MERCK (*Chem. Centr.*, 1897, i, 476; from *Ber. u. d. Jahr.*, 1896. Compare Petit and Polonowsky, *Abstr.*, 1897, i, 581—582).—The author has been unable to confirm Harnack's statement that pure pilocarpidine may be obtained by means of the platinochloride. He finds also that the aurochloride is slightly soluble in water; this salt, $C_{10}H_{14}N_2O_2 \cdot HAuCl_4$, which melts at 125—128° and crystallises from glacial acetic acid in needles or prisms, is decomposed by hydrogen sulphide, yielding pilocarpidine hydrochloride, whose platinochloride, $(C_{10}H_{14}N_2O_2)_2 \cdot H_2PtCl_6 + 4H_2O$, melts at 100°; the anhydrous salt melts at 186—190°; Harnack states that the platinochloride decomposes at 130°. Pure pilocarpidine, which the author obtains from the aurochloride, is an alkaline syrup rather easily soluble in water, and has a specific rotatory power $[\alpha]_D = +72^\circ$. It is decomposed by concentrated potassium hydroxide solution at 200° with liberation of dimethylamine. Hardy and Calmels state that they have obtained pilocarpine from pilocarpidine by means of methylic iodide, but the author has prepared pilocarpidine methiodide, converted it into the corresponding chloride, and obtained a platinochloride, $(C_{11}H_{16}N_2O_2)_2 \cdot H_2PtCl_6 + 4H_2O$, which softens at 175°, melts at 178°, and is not identical with pilocarpine hydrochloride. E. W. W.

Carpaine. By J. J. L. VAN RIJN (*Chem. Centr.*, 1897, i, 985; from *Ned. Tijdschr. Pharm.*, 9, 47—63).—This is largely a repetition of the preliminary paper (compare *Abstr.*, 1897, i, 647). Since methylcarpaine, $C_{14}H_{24}MeNO_2$, reacts with benzoic chloride, it probably contains a hydroxyl group. The author has also obtained a glucoside, which he names *carposide*, from papaya leaves; this crystallises in colourless needles, and is insoluble in ether but soluble in alcohol, and in water. Its aqueous solution reduces Fehling's solution only after boiling with dilute sulphuric acid. E. W. W.

Curara and Curara Alkaloids. By RUDOLF BOEHM (*Arch. Pharm.*, 1897, 235, 660—684).—The curara alkaloids may be divided into two classes. Those of the first series, like curine, are partly crystalline and partly amorphous, soluble in water with difficulty, and are precipitated from solutions by ammonia. They are soluble in ether and give, without exception, voluminous precipitates with metaphosphoric acid. The characteristic toxic effect of curara is shown very slightly or not at all by them. The members of the second series are, like curarine, amorphous, yellowish-red substances, easily soluble in water, but insoluble in ether, and cannot be precipitated from solutions of their salts by ammonium hydroxide or other alkalis. The halogen of their haloid

salts can only be completely removed by silver oxide and the alkaloids themselves show the most marked curara action.

Paracurara, or tube curara, is imported in bamboo tubes, and is the variety now usually met with in commerce. It is a dark brown mass impregnated with well-defined, yellowish coloured crystals of quercitol, often 2 cm. long. It contains 11—14 per cent. of water, and about 12 per cent. of ash, consisting for the most part of the carbonates, phosphates, and chlorides of potassium, calcium, and magnesium. Its toxic dose for rabbits is 0.005—0.01 gram per 1 kilo. body weight.

Its solutions are precipitated by concentrated nitric acid, and at the same time a red coloration is produced which is intensified on heating. Metaphosphoric acid causes a voluminous precipitate, as do also the alkalis, many metallic salts, and all alkaloid reagents.

Curine, $C_{18}H_{19}NO_3$ (Abstr., 1887, 1125) is contained in paracurara to the extent of 12—15 per cent. It may be isolated by extracting the raw material with water, precipitating the solution with aqueous ammonia, and extracting with dilute alcohol. It crystallises from benzene in colourless, glistening, four-sided prisms melting at 161° , from ethylic alcohol in crystals melting at 159 — 163° , and from methylic alcohol in crystals melting at 212° . In the first two cases, the crystals contain one molecule of the solvent, which may be eliminated by heating to 180° in a stream of hydrogen. Curine is soluble in dilute acids to form a colourless solution tasting at first sweet and then bitter; it also dissolves in concentrated alkalis, but is insoluble in water. When moistened with sulphovanadic acid, it dissolves, giving a black colour, but this soon becomes dark blue on the edges and then clear red. Metaphosphoric acid and all the alkaloidal reagents cause precipitation; ammoniacal silver nitrate solution is reduced, but no red colour is obtained with Millon's reagent.

The *platinochloride* is an amorphous, yellow powder insoluble in water and alcohol; the *methiodide* crystallises in slender, yellow needles melting at 252 — 253° ; and the *methochloride* in colourless, rhombic plates. When the latter is acted on with silver oxide, the ammonium hydroxide base of quaternary methylcurine is obtained as an amorphous, yellowish-red powder.

Curine contains one methoxy-group; it cannot be benzoylated, but on treatment with methylic iodide and caustic potash the *methylic ether* of methylcurine is formed, as a non-crystalline substance, of which the platinochloride and aurochloride were analysed. When fused with potash, curine yields amino-bases and protocathechuic acid; and when distilled with soda lime or zinc dust, the principal product is trimethylamine, and also a substance giving the characteristic reactions for paraquinoneanisoil, showing the existence of a methoxyquinoline ring in curine.

Paracurarine (tubocurarine).—The filtrate, after extracting curine, contains quercitol and curarine, obtained by precipitation with mercuric chloride, &c. It is an amorphous, reddish-yellow substance, forming 9—11 per cent. of the raw curara. It is soluble in water and alcohol, forming a red solution with a green fluorescence, and is not identical with the previously known curarine isolated from calabash-curara. In its behaviour towards reagents, it resembles curine,

except that it is not precipitated by the alkali phosphates. The *platinochloride* and *hydriodide* are yellow, amorphous powders. Tubocurarine contains one methoxy-group, but, unlike curine, is not acted on by methylic iodide, and is therefore not a tertiary base.

Calabash-curara used to be the common variety, and is that to which earlier investigations, as a rule, refer, but it is now seldom met with; it was sent over in calabashes. It is a hard, dark brown substance, with a peculiar smell and a very bitter taste. Its watery solution, which is slightly acid, is coloured purple by concentrated sulphuric and nitric acids. The active principle is curarine, obtained together with minute quantities of a second alkaloid by precipitating an aqueous extract of the raw material with platinic chloride, decomposing with hydrogen sulphide, and extracting with a mixture of alcohol and chloroform. It forms hard, glistening, garnet-red laminæ, decomposing and giving off a smell of trimethylamine when heated at 150° . It is odourless, has an intensely bitter taste; and gives blue to violet colour reactions with concentrated sulphuric, nitric, or sulphovanadic acid. The *platinochloride* is an amorphous, strongly electrical powder, decomposing without melting when heated, and the *hydriodide* is the only compound which shows a tendency to crystallise.

A third variety of curara is sent over in small jars of unburnt clay; it is a dry, blackish-brown substance, and differs widely in the amount of active principle which it contains. The following substances have been extracted from it.

Protocurine, $C_{20}H_{23}NO_3$, crystallises from methylic alcohol in colourless, hair-like needles, which, on heating, turn brown at 160° and melt at 306° with decomposition. It gives no characteristic colour reactions. It yields crystalline salts possessing a bitter taste.

Protocuridine.—The free base is quite insoluble, but may be purified by boiling repeatedly with chloroform, when it is obtained in the form of hard, colourless, prismatic crystals melting at 274 – 276° ; it is easily soluble in dilute acids, is precipitated by the usual alkaloidal reagents, but gives no characteristic colour reactions. The *sulphate* and *platinochloride* are crystalline substances.

Protocurarine is an amorphous, red powder, easily soluble in water and alcohol, and is more poisonous than the other curarines. Its salts are inactive. It gives characteristic colour reactions with sulphuric, nitric, and sulphovanadic acids, and reduces ammoniacal silver nitrate solution.

A. W. C.

Enzymes. By WACŁAW VON MORACZEWSKI (*Pflüger's Archiv.*, 1897, 69, 32–75).—The question is investigated whether various enzymes (diastase, pepsin, fat-splitting enzymes, &c.) require calcium salts for their activity to be manifested in the same way as rennin does. It was found that no method of precipitating calcium salts inhibits the activity of these enzymes. The presence of calcium salts is favourable to their action, and in a few cases (ptyalin and diastase) the removal of calcium salts weakens their activity, but even this action is inconstant.

W. D. H.

Influence of Heat on Diastatic Ferments. By ANGELO PUGLIESE (*Pflüger's Archiv.*, 1897, 69, 115–131).—The research is

directed to the question whether diastase of vegetable origin is the same ferment as the diastatic enzymes of animals. Although it is regarded as probable that the enzymes are different, the problem is one which cannot yet be solved. Certainly, no difference in relationship to the temperature at which they are most active could be discovered.

W. D. H.

Chemical Nature of Diastase. By THOMAS B. OSBORNE (*Ber.*, 1898, 31, 254—259. Compare *Abstr.*, 1896, i, 398, and Wróblewski, this vol., i, 54).—The author considers that the reason why Wróblewski's diastase did not coagulate on warming to 50—60°, was on account of the small quantity of true diastase present. It has already been shown that dilute solutions of malt albumin and of other vegetable proteids do not coagulate. That Wróblewski's preparation was not so pure as the author's was proved by comparing the amount of maltose obtained by the aid of each. It is also stated in reply to Wróblewski that the author's preparations were quite free from the carbohydrate, araban.

J. J. S.

Betulase, an Enzyme contained in *Betula Lenta*. By AUGUST SCHNEEGANS (*Chem. Centr.*, 1897, i, 326; from *Journ. Pharm. d'Als.-Lorr.*, 1896, No. 17).—Gaultherin, the glucoside present in the bark of *Betula lenta*, on hydrolysis yields a carbohydrate and methylic salicylate, and by macerating the powdered bark of *Betula lenta* during four weeks with glycerol, the author has extracted an enzyme, *betulase*, capable of rapidly effecting the same change. On adding alcohol to its glycerol solution, betulase is precipitated as a greyish-white powder, the yield being about 0.1 per cent. of the weight of bark taken. The hydrolytic power of betulase is not affected by exposing it for a long period to the air, or by long drying in a desiccator, or even by heating it for several hours at 130°; on the other hand, an aqueous solution of the enzyme rapidly loses its hydrolytic power, especially on being heated. It cannot be dialysed, and becomes turbid when heated or when a mineral acid is added to it. The hydrolytic power of betulase seems to be increased by the presence of small quantities of alkalis or mineral acids, but is diminished by the presence of tannic, picric, or tartaric acid, or of ferric chloride, mercurous nitrate or lead acetate. Mercuric chloride and the sulphates of copper, iron, and zinc are without action. An aqueous solution of betulase does not give a blue coloration with guaiacol, even in presence of hydrogen peroxide; it does not convert starch into sugar, or dissolve albumin or fibrin; neither does it hydrolyse amygdalin, phloridzin, nor salicin. Diastase, emulsin, papayotin, pepsin, or ptyalin do not act on gaultherin. In *Betula lenta*, as in the bitter almond, a glucoside and an enzyme capable of hydrolysing it exist together.

W. A. D.

Action of Rennin. By G. LÖRCHER (*Pflüger's Archiv.*, 1897, 69, 141—198).—The research gives an account of various methods of obtaining rennin and its zymogen, and of various agencies which modify its activity.

Boiled milk is coagulated more slowly by rennin than fresh milk. The activity of the ferment is diminished by both acids and alkalis,

but an acid reaction raises the resistance to temperature of the ferment.

Rennin is also more resistant to heat in glycerol than in water; the ferment acts between 10° and 60° , but a temperature of 60 — 70° destroys its activity. The rennin from the frog is active at lower temperatures than that of the calf or human stomach.

The amount of the enzyme is very small during fasting, and still more so in the state of digestion; the amount of the zymogen is, however, considerable.

W. D. H.

Classification of Proteids. By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1897, 30, 3045—3052).—The author gives a scheme for the classification of proteids and allied substances, for which reference must be made to the original.

Halogen Derivatives of Proteids, and their Physiological Relationships. By F. BLUM (*Chem. Centr.*, 1897, i, 181—182; from *Munch. med. Woch.* 43, 1099).—Stable compounds of proteid are obtainable with iodine, bromine, and chlorine. The iodine compound is stated to be physiologically useful after thyroidectomy, the bromine compound in epilepsy, and the chlorine compound in catarrh and cancer of the stomach.

W. D. H.

Halogen Derivatives of Albumin By F. BLUM and WILHELM VAUBEL (*J. pr. Chem.*, 1897, [ii], 56, 393—396. Compare Loew and Takabayashi, *Abstr.*, 1897, i, 648; Liebrecht, *ibid.*; Hopkins, this vol., i, 54; Hopkins and Brook, *ibid.*, 99).—When a casein solution is warmed with tincture of iodine or with bromine, or treated with chlorine in the cold, and the product is then boiled with aqueous alkali until all the sulphur, and as much halogen as possible, have been removed, the residual product, after precipitation with mineral acids or acetic acid, still contains 2.4—2.6 per cent. of chlorine, 4.8—5.0 per cent. of bromine, or up to 9.7 per cent. of iodine respectively. These numbers correspond to a molecular weight of about 1400 for the product, assuming only one atom of the halogen to be present in the molecule. The amount of ash was very variable; part of the product dissolved in 90 per cent. alcohol and part did not; during the boiling with alkali, ammonia and other gases were evolved, and a smell of thiocarbimides and of trimethylamine was sometimes noticed. When the product of the action of the halogens is heated with 10 per cent. sulphuric acid, instead of with alkali, some halogen is still firmly retained; in neither case is it removed by boiling with silver nitrate. Strong sulphuric acid, and other oxidising agents, do remove it, however. With other proteids—egg-albumin, serum-albumin, protogen, myosin, Witte's peptone, somatose, albumoses, gelatins, &c.—similar results are obtained.

C. F. B.

Action of Formaldehyde on Albumin. By A. BACH (*Chem. Centr.*, 1897, i, 420; from *Mon. Sci.*, [iv], 11, i, 157—159. Compare *Abstr.*, 1893, ii, 483).—The author considers that the formaldehyde present in plants is a decomposition product of carbonic anhydride; it seems to be protected from the action of the oxygen liberated simultaneously. To ascertain the cause of this immunity from oxidation, the action of formaldehyde on an aqueous solution of albumin was

studied. A product soluble in water was obtained, the aqueous solution of which was not coagulated by heat, and was less easily precipitable by 95 per cent. alcohol than that of ordinary albumin. If shreds of albumin are dried either in bright sunlight, or at a low temperature, and then dissolved in water, non-coagulable solutions are obtained; in the former case, the solution can be rendered coagulable by the addition of a few drops of acetic acid; in the latter case, by passing a stream of carbonic anhydride.

W. A. D.

Separation of Albumoses and Peptone.—By ERNST P. PICK (*Zeit. physiol. Chem.*, 1897, 24, 246—275).—A detailed account of experiments on the fractional precipitation with ammonium sulphate of solutions of Witte's "peptone." The properties of the various fractions are described, and the general conclusion drawn that Witte's peptone contains several albumoses and peptones. Further details, however, are promised regarding their characters and identification.

W. D. H.

New Colloidal Substances Analogous to Proteids derived from a Nucleo-albumin. By JOHN W. PICKERING (*Compt. rend.*, 1897, 125, 963—965).—Nucleoalbumin prepared from the thymus of the sheep by Halliburton's method was heated with anhydrous calcium chloride in sealed tubes at 150° for 6 hours. The product is a brown, crystalline powder which has not the properties of proteids, although it still gives a violet coloration with potassium hydroxide and cupric sulphate. It has no lævorotatory power, and does not produce intravascular coagulation. When this product is heated in sealed tubes at 125° for 4 hours with phosphorus pentachloride, it is partially converted into a colloid which, after purification by dialysis, is identical in appearance, chemical reactions, and physiological effects with the synthetic colloids obtained by Grimaux.

C. H. B.

Chemistry of Hæmoglobin. By JOHN S. HALDANE (*J. physiol.*, 1898, 22, 298—306).—When potassium ferricyanide is added to solutions of oxyhæmoglobin or carbonic oxide hæmoglobin, or to blood laked by the addition of water, the gas combined with the hæmoglobin is set free, while methæmoglobin is formed. The oxygen of the blood can be rapidly and accurately determined without the use of the air-pump, by taking advantage of this reaction; a somewhat modified Dupré urea apparatus may be used for this purpose.

W. D. H.

Absorption of Violet and Ultra-violet Rays by Hæmoglobin and its Derivatives. By ARTHUR GAMGEE (*Zeit. Biol.*, 1897, 34, *Jubelband*, 505—528).—A full account, illustrated with photographs of spectra, of researches which have been previously published (*Abstr.*, 1896, i, 713).

W. D. H.

Organic Chemistry.

Methyldiethylethylene. By MICHAEL SAYTZEFF, jun. (*J. pr. Chem.*, 1898, [ii], 57, 38—43).—The formation of the heptylene obtained by Baratéeff and Saytzeff (*Abstr.*, 1887, 353) as one of the oxidation products of triethylcarbinol, was probably due to the dehydrating influence of the sulphuric acid used in the oxidising mixture; it seems to be a *methyldiethylethylene*, $\text{CET}_2\text{:CHMe}$, and can be prepared by heating triethylcarbinol (1 mol.), with oxalic acid (1 mol.), which acts as a dehydrating agent (compare Cahours and Demarçay, *Abstr.*, 1878, 653). The hydrocarbon is a colourless liquid which boils at $97\text{--}98^\circ$, and has a sp. gr. = 0.72285 at $20^\circ/20^\circ$, and = 0.72225 at $20^\circ/0^\circ$; on oxidation with potassium permanganate, no trace of a glycol can be obtained, acetic and propionic acids being formed, together with a small quantity of triethylcarbinol. The author concludes that the latter substance is first formed by the addition of $1\text{H}_2\text{O}$ to the methyldiethylethylene, and that the acetic and propionic acids result from its oxidation. W. A. D.

Aliphatic Nitroso-compounds. By OSCAR PILOTY (*Ber.*, 1898, 31, 452—457. Compare *Abstr.*, this vol., i, 117.)—When acetoxime is dissolved in water and treated with bromine in presence of pyridine, *2-bromo-2-nitrosopropane*, $\text{CBrMe}_2\text{:NO}$, is formed as a deep blue, mobile liquid, which has an extremely unpleasant, pungent odour; it boils and decomposes at 83° , but can be distilled at 12.5° under a pressure of 26 mm. without alteration. It dissolves readily in benzene, alcohol, &c., but is insoluble in water, and when kept decomposes, forming acetoxime hydrobromide and a liquid which is insoluble in ether, and gives a vapour which has an extremely irritating effect on the mucous membrane. The molecular weight was determined by the freezing point method in benzene solution. The isomeric acetoxime hypobromite, $\text{CMe}_2\text{:N:OBr}$, has not been obtained, but the corresponding hypochlorite is known, and is a colourless liquid. The author concludes from these facts that the blue colour is associated with the presence of the nitroso-group, and that, therefore, the pseudonitroles must also be considered to contain this group.

Several solid nitroso-compounds, such as $\text{C}(\text{CH}_2\text{:OAc})_3\text{:NO}$, and nitroso-octane (see the following abstract), which are colourless in the crystalline state, form colourless solutions in benzene at a low temperature, whilst if the temperature be allowed to rise slightly, the solution becomes blue. A determination of the freezing point of these solutions shows that, in the colourless solution, the nitroso-compound has twice the molecular weight that it has in the blue solution.

A. H.

Nitroso-octane. By OSCAR PILOTY and OTTO RUFF (*Ber.*, 1898, 31, 457—458. Compare the foregoing abstract).—When nitrodi-isobutyl, $\text{NO}_2\text{:CMe}_2\text{:CH}_2\text{:CH}_2\text{:CHMe}_2$, is reduced with aluminium amalgam in presence of ether, it is converted into *2-nitroso-2:5-dimethylhexane*, $\text{NO:CMe}_2\text{:CH}_2\text{:CH}_2\text{:CHMe}_2$, which crystallises in compact, colourless,

prismatic plates melting at 54° to a deep blue liquid; it sublimes, without decomposition, above its melting point, and is insoluble in water, acids, and alkalis.

Regularities in the Boiling Points of Isomeric Aliphatic Compounds. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1898, 31, 313—314).—A reply to Naumann (this vol., i, 221). M. O. F.

Preparation of Absolute Alcohol by means of Calcium Carbide. By PAUL YVON (*Compt. rend.*, 1897, 125, 1181—1182).—When calcium carbide is added to alcohol which contains water, the carbide is attacked with liberation of acetylene so long as any water remains undecomposed. This reaction can be used for the detection of water in alcohol; acetylene is liberated, and the liquid when shaken becomes turbid, owing to the presence of calcium hydroxide. It can also be employed for the preparation of anhydrous alcohol; for this purpose, alcohol of 90° or 95° is mixed with about one-quarter its weight of the coarsely granulated carbide, well shaken from time to time during 2 or 3 hours, allowed to remain 12 hours, and then decanted and distilled. The first portions of the distillate contain some dissolved acetylene and may be collected separately, or the entire distillate may be shaken with anhydrous cupric sulphate, and redistilled without previously separating the copper acetylide. C. H. B.

Alkyl sulphites. By ARTHUR ROSENHEIM and OTTO LIEBKNECHT (*Ber.*, 1898, 31, 405—414).—Contrary to the statement of Warlitz (*Annalen*, 1867, 143, 72), ethylic sulphite, $\text{SO}(\text{OEt})_2$, is decomposed only with extreme slowness by 20 per cent. aqueous potash, and the product is not potassium ethylic sulphite, $\text{OEt}\cdot\text{SO}\cdot\text{OK}$, but potassium ethylsulphonate, $\text{Et}\cdot\text{SO}_2\cdot\text{OK}$, for it yields no sulphurous anhydride when treated with mineral acids. True alkyl sulphites, which the authors formulate as $\text{M}'\cdot\text{SO}_2\cdot\text{OR}$ [$\text{R} = \text{Me}, \text{Et}$; $\text{M}' = \text{Na}, \text{K}$], can be obtained by passing the calculated amount of sulphurous anhydride into alcoholic sodium or potassium methoxide or ethoxide (compare Szarvasy, *Abstr.*, 1897, i, 585). Sodium methylic sulphite will keep for weeks in a well stoppered bottle; the ethylic salt decomposes in about an hour, with evolution of sulphurous anhydride, and potassium ethylic sulphite decomposes as soon as it has become dry, although both of these salts are comparatively stable when in contact with alcohol. Neither propylic, amylic, nor phenylic sulphites can be obtained by this method. The alkyl sulphites exhibit very different reactions from those of the isomeric alkylsulphonates; for example, they are decomposed, even by dilute mineral acids, sulphurous anhydride being evolved. Sodium methylic sulphite is stable in aqueous solution at 0° , but at 25° it is decomposed into methylic alcohol and sodium hydrogen sulphite; the ethylic sulphite undergoes this decomposition even more readily. When heated with ethylic iodide and absolute alcohol at 150° , sodium ethylic sulphite undergoes transformation into the ethylsulphonate; a crystalline product is obtained which has the composition $4\text{EtSO}_3\text{Na}\cdot\text{NaI}$, and can also be prepared by the direct action of sodium iodide on sodium ethylsulphonate.

The ease with which the alkyl sulphites described are hydrolysed

as compared with the difficulty experienced in hydrolysing ethylic sulphite, $\text{SO}_2(\text{OEt})_2$, leads to the conclusion that they cannot, like this last substance, have the symmetrical structure $\text{OM} \cdot \text{SO} \cdot \text{OR}$, but must rather be formulated as $\text{M} \cdot \text{SO}_2 \cdot \text{OR}$.
C. F. B.

Methyltertiarybutylallylcarbinol. By AL. GNEDIN (*J. pr. Chem.* 1898, [ii], 57, 104—111).—*Methyltertiarybutylallylcarbinol*, obtained by the action of zinc and allylic iodide on pinacolin, is a colourless, mobile liquid smelling strongly of camphor, boils at 168.4° (corr.), solidifies on cooling to four-sided prisms melting at -7° , and has a sp. gr. = 0.85639 at $20^\circ/20^\circ$. Although it contains an asymmetric carbon atom, it is optically inactive.

On oxidation with potassium permanganate, it is converted first into a *hydroxy*-derivative, $\text{C}_9\text{H}_{20}\text{O}_3$, crystallising in triclinic plates, and melting at 87 — 88° , and on further oxidation into an acid having the composition of β -methyltertiarybutylethylenelactic acid.

A. W. C.

Tertiary Nitroisobutylenic Glycol. By GIUSEPPE CESÀRO (*Chem. Centr.*, 1897, ii, 179; from *Bull. Acad. roy. Belg.*, [iii], 33, 323—333).—The author gives the results of a crystallographic examination of the large yellow, and small colourless crystals of tertiary nitroisobutylenic glycol prepared by Henry (Abstr., 1896, i, 4). When heated, this compound loses its crystalline form before melting, melts at 140° , and on cooling suddenly, crystallises at 57° ; on again heating and cooling, the same phenomena are exhibited.

E. W. W.

Trihydric Alcohol obtained from Dipropylallylcarbinol. By ALEXIS BOGORODSKY (*J. pr. Chem.*, 1898, [ii], 57, 35—38).—1-Dipropyl-1:3:4-butetriol, $\text{OH} \cdot \text{CPr}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, obtained on oxidising dipropylallylcarbinol (1 mol.) with aqueous potassium permanganate ($1\frac{1}{2}$ mols.), is a viscid, colourless liquid, which is easily soluble in water and alcohol, but only sparingly in ether. On being heated with acetic anhydride, it yields a mixture of its triacetyl compound, and the diacetate of an unsaturated glycol, $\text{CPr}_2 \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$; these products were, however, not separated.

W. A. D.

Formaldehyde or Methylene Derivatives of certain Polyhydric Alcohols and Acids of the Sugar Group. By K. WEBER and BERNHARD TOLLENS (*Annalen*, 1898, 299, 316—340).—A more detailed account of work which has already been published (see this vol., i, 60).
M. O. F.

Fermentation of Cellulose. By V. OMELIANSKI (*Compt. rend.*, 1897, 125, 1131—1133).—Pure paper was allowed to ferment in presence of calcium carbonate at a temperature of about 35° for 13 months. The products obtained from 3.4743 grams of paper were:—acids of the acetic series, 2.2402 grams; carbonic anhydride, 0.9722 gram; and hydrogen, 0.0138 gram. The acids were chiefly acetic acid and butyric acid, the ratio of the former to the latter being 1.7 : 1. Small quantities of valeric acid, higher alcohols, and odorous products were formed.

The absence of methane from the products of fermentation is remark-

able, but the formation of this gas seems to be due to a special organism readily distinguishable from the ferment that produces the fatty acids. This organism is at present under investigation. C. H. B.

Ethylnitramine and its Derivatives. By HERM. UMBROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1897, 16, 385—400. Compare Abstr., 1889, 493).—To prepare *diethyldinitro-oxamide*, 5 grams of diethyloxamide are gradually added to 20 c.c. of pure, colourless nitric acid (obtained by distilling nitric acid with sulphuric acid under diminished pressure). The mixture is allowed to remain in a dry atmosphere for several days at the ordinary temperature, and is then poured into a mixture of ice and water. It is extracted with ether, the ethereal solution agitated with dilute sodium carbonate, and then dried with potassium carbonate. The solid residue from the ethereal solution is recrystallised from alcohol; the yield is usually about 93 per cent. of the theoretical. Diethyldinitro-oxamide melts at 35° , is readily soluble in ether, but is only sparingly soluble in light petroleum or cold alcohol. Attempts to nitrate diethyloxamide by the aid of a mixture of nitric and sulphuric acids did not give good results.

The finely powdered nitro-derivative (28 grams) is gradually added to strong aqueous ammonia (90 c.c.), and the temperature is moderated by surrounding the vessel with cold water; after some time, the mixture is filtered, the residue washed, and the colourless filtrate warmed on the water bath; when cold, sulphuric acid (10 per cent.) is added until the solution gives a blue colour with Congo-red paper. The solution is then extracted with ether, and the residue from the ethereal extract, after keeping for some time over sulphuric acid in a vacuum, consists of pure ethylnitramine. Its sp. gr. at $15^{\circ} = 1.1675$, and when placed in a freezing mixture it solidifies to rhombic plates melting at 6° ; it is odourless, and has an acid reaction.

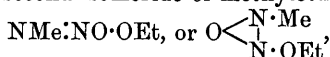
The *potassium, sodium, lithium*, EtNLiNO_2 , *silver, barium*, $[\text{EtN}\cdot\text{NO}_2]_2\text{Ba} + \text{H}_2\text{O}$, *zinc* $[\text{EtN}\cdot\text{NO}_2]_2\text{Zn} + 2\text{H}_2\text{O}$, *cobalt*, $+ 2\text{H}_2\text{O}$, *nickel, cupric*, $+ 2\text{H}_2\text{O}$, and *mercuric* compounds are described. The zinc, nickel, copper, and mercury derivatives were obtained by double decomposition from the barium compound, since they are decomposed when their aqueous solutions are boiled.

Normal methylethylnitramine, identical with van Dissel's compound (*Rec. Trav. Chim.*, 1894, 13, 327), is obtained when the potassium derivative (25 grams) is mixed with methylic iodide (30 grams) and methylic alcohol (90 grams), the mixture being first allowed to remain at the ordinary temperature during 2 days, and then boiled on the water bath for 6 hours; it distils at 90.5° under a pressure of 23 mm., and its sp. gr. $= 1.1012$ at 15° ; it does not yield a coloration with an acetic acid solution of α -naphthylamine, and does not react with sulphuric acid. When heated in sealed tubes with thirty times its weight of aqueous potash (10 per cent.) for 12 hours at 100° , it is completely decomposed, yielding nitrous acid and ethylamine, which was tested for by Romburg's method. Diethylnitramine may be prepared in a similar manner by the aid of ethylic iodide; it has previously been obtained from unsymmetrical diethylcarbamide (*Rec. Trav. Chim.*,

1887, 6, 149). The authors confirm van Erp's statement that diethylnitramine is practically unacted on when boiled with aqueous potash for some 5 hours. When heated with thirty times its weight of 10 per cent. aqueous potash at 150–160° for 4 hours, complete decomposition ensues, the chief products being ethylamine, nitrous acid, and resinous matter. *Isomethylethylnitramine* is the chief product formed when the silver derivative of ethylnitramine (97 grams) is treated with methylic iodide (69 grams) and absolute ether (500 c.c.); it is also probably formed in small quantity in the preparation of the normal compound. After repeated fractionation under diminished pressure, it is obtained in the form of a colourless liquid boiling at 36–38° under a pressure of 20 mm., and having a sp. gr. = 1.0415 at 15°; it yields a coloration with α -naphthylamine acetate, and reacts vigorously with sulphuric acid. When heated at 100° in sealed tubes with aqueous potash (10 per cent.), the products are nitrogen, methylic alcohol, and a red resin, probably formed by the action of the alkali on acetaldehyde, one of the primary decomposition products. *Isodiethylnitramine* boils at 46–50° under a pressure of 18 mm., has a sp. gr. = 1.000 at 15°, and resembles the isomethyl derivative in all its reactions. J. J. S.

Two Isomerides of Methylethylnitramine. By HERM. UMBROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1897, 16, 401–410. Compare preceding abstract.).—The compound formed by the introduction of a methyl group into ethylnitramine by the action of methylic iodide on its silver derivative, is supposed to have the constitution $\text{NEt}:\text{NO}:\text{OMe}$ or $\text{O} \begin{smallmatrix} \text{N} \cdot \text{Et} \\ | \\ \text{N} \cdot \text{OMe} \end{smallmatrix}$. When heated in a Pfungst tube

at 100° for 7 hours with aqueous potash (10 per cent.), it yields nitrogen and methylic alcohol, together with a small quantity of a substance somewhat richer in carbon, probably dimethylacetal, formed by the action of the methylic alcohol on acetaldehyde. A red, resinous substance is also formed, probably by the action of the alkali on acetaldehyde. The second isomeride of methylethylnitramine,



is obtained by the action of ethylic iodide dissolved in absolute ether on methylnitramine. After several rectifications under diminished pressure, it boils at 35° under a pressure of 16 mm., and its sp. gr. = 1.044 at 15°. A substance boiling at 78° under a pressure of 18 mm., and melting at about 6°, was obtained as a bye-product. The second isomeride of methylethylnitramine, when heated with aqueous potash in exactly the same manner as the preceding compound, gave nitrogen and ethylic alcohol; methylic alcohol and formic acid were also produced, but in smaller quantities. The methylic alcohol was tested for by a 12 per cent. solution of chromic anhydride, which readily reacts with methylic alcohol, yielding carbonic anhydride, but which gives practically no gas with ethylic alcohol. J. J. S.

Two Inactive 2:4-Diamidopentanes. By CARL D. HARRIES and TAMEMASA HAGA (*Ber.*, 1898, 31, 550–551).—When acetylacetone-dioxime is reduced with sodium and boiling alcohol, a 2:4-diamidopen-

tane, $\text{CH}_2 \cdot (\text{CHMe} \cdot \text{NH}_2)_2$, is formed, which, after drying with barium hydroxide, distils at $41-42^\circ$ under 11—12 mm. pressure; it is a colourless liquid and fumes in the air. Its *hydrochloride*, $\text{C}_5\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$, *hydrobromide*, *platinochloride*, and *aurochloride* are well-defined, crystalline compounds. The *diacetyl* derivative crystallises in large, thick prisms, melts at 163° , and is practically insoluble in ether. The *dibenzoyl* derivative crystallises in plates and melts at 189° .

When the dioxime is reduced with sodium amalgam and 80 per cent. acetic acid in the cold, the product is a mixture of the above-mentioned diamidopentane and of an isomeride; they are best separated in the form of their diacetyl derivatives. The one already described is a crystalline substance, whereas the isomeric diacetyl derivative is a syrup. When this syrup is hydrolysed with concentrated hydrochloric acid at $150-160^\circ$ it is converted into the isomeric 2:4-diamidopentane and acetic acid. On evaporating the solution, a hygroscopic *hydrochloride* of the base is obtained, which, on benzoylating, yields a *dibenzoyl* derivative. This melts at the same temperature as the dibenzoyl derivative of the first mentioned 2:4-diamidopropane, but the two are not identical, since a mixture of them melts at 158° . The isomeric base, after drying over barium hydroxide, boils at $29-30^\circ$ under a pressure of 9—10 mm.

J. J. S.

New Formation of Trioxymethylene. By GIUSEPPE GRASSI-CRISTALDI (*Gazzetta*, 1897, 27, ii, 502—505).—On passing the vapour of monochloroacetic acid through a glass tube kept at a low red heat, hydrogen chloride and carbonic oxide are evolved, and a mixture of formic acid, symmetrical dichloromethylic ether, and trioxymethylene is condensed.

It may be supposed that chloroacetic acid decomposes on heating in a similar manner to hydroxycarboxylic acids, with elimination of carbonic oxide, hydrogen chloride, and formaldehyde; the latter in part polymerises, giving trioxymethylene, and in part combines with hydrogen chloride, giving the chlorhydrin $\text{CH}_2\text{Cl} \cdot \text{OH}$, which, by loss of water, yields dichloromethylic ether, $(\text{CH}_2\text{Cl})_2\text{O}$. It may also be supposed that the chloroacetic acid first decomposes into carbonic oxide and the chlorhydrin of formaldehyde which, by loss of hydrogen chloride, gives formaldehyde and by loss of water yields dichloromethylic ether. The formic acid produced during the heating is regarded as an oxidation product.

W. J. P.

β -Nitrosoketones. By CARL D. HARRIES and LUDWIG JABLONSKY (*Ber.*, 1898, 31, 549—550).—When diacetonehydroxylamine (this vol., i, 123) is oxidised in chloroform solution with yellow mercuric oxide, β -nitrosoisopropylacetone, $\text{NO} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac}$, is formed; it crystallises in long prisms and melts at $75-76^\circ$, yielding a deep blue liquid. The oxidation of diacetonehydroxylamine to a nitroso-compound establishes with certainty the constitution of the former, since Piloty and Ruff (this vol., i, 223) have shown that only tertiary aliphatic hydroxylamines can be thus oxidised. Dihydroxylaminotriacetone, when oxidised in a similar manner, yields *dinitrosodi-isopropylacetone* [*dinitrosodi-isobutyl ketone*], $\text{CO}(\text{CH}_2 \cdot \text{CMe}_2\text{NO})_2$, melting at $132-133^\circ$.

J. J. S.

Isolation of Amido-acids. By N. A. ORLOFF (*Chem. Centr.*, 1897, ii, 192—193; from *Pharm. Zeit. Russ.*, 36, 285—289, 301—303).—The author recommends the nickel salts of amido-acids as a convenient means of separating these acids from the decomposition products of proteids such as those contained in plants, and describes the following compounds.

The *nickel salt of alanine*, $(C_3H_7NO_2)_2Ni + 4H_2O$, prepared by boiling an aqueous solution of alanine with nickel carbonate for 1—1½ hours, forms blue crystals, and loses its water of crystallisation at 108—110°; 100 parts of a saturated aqueous solution contain 0.76 parts of the salt. The *nickel salt of glycocine*, $(C_2H_4NO_2)_2Ni + 2H_2O$, is prepared in a similar manner to the preceding compound, and, like it, is easily soluble in hot water; 100 parts of a saturated aqueous solution at the ordinary temperature contain 3.35 parts of the salt. Leucine does not form a nickel salt when boiled with nickel carbonate or hydroxide. Asparagine yields an easily soluble, amorphous, nickel salt. Generally speaking, those amido-acids whose copper salts are easily soluble and difficult to crystallise, form easily crystallisable nickel salts.

The author has isolated tyrosine, glycocine, and leucine from the decomposition products obtained by heating gelatin and albumin respectively with sulphuric acid of 50—80 per cent. strength for ½—2 hours at a temperature below the boiling point. E. W. W.

Action of Cyanacetic Acid on Isovaleraldehyde and Propaldehyde. By ERNST STRASSMANN (*Monatsh.*, 1897, 18, 722—736).—When cyanacetic acid (1 mol.) is heated with isovaleraldehyde (1 mol.) in a sealed tube during 1—2 hours at 106°, a *cyanisoheptenoic acid*, $CH_2Pr^{\beta}:CH:C(CN)\cdot COOH$ or $CHPr^{\beta}:CH\cdot CH(CN)\cdot COOH$, is formed, which crystallises from light petroleum containing ether, in white, deliquescent needles, melts at 53°, and is easily soluble in ether and water. The *silver salt* is very unstable, whilst the *calcium salt*, $(C_8H_{10}O_2N)_2Ca + 2\frac{1}{2}H_2O$, crystallises when its aqueous solution is evaporated in a vacuum, although it is decomposed when the latter is heated. On being heated with aqueous potash, the cyano-acid is resolved into ammonia, malonic acid, and isovaleraldehyde and its condensation products; when distilled alone, carbonic anhydride and *βγ-isoeptenenitrile*, $CHPr^{\beta}:CH\cdot CH_2\cdot CN$, are formed. The latter boils at 80° under a pressure of 18 mm., and at 175° (corr.) under ordinary pressure, and combines readily with bromine, forming a *dibromide*, $C_7H_{11}NBr_2$, which crystallises in iridescent, white plates and melts at 67°. When heated with 10 per cent. aqueous potash, the nitrile is converted into *βγ-isoeptenoic acid*, $CHPr^{\beta}:CH\cdot CH_2\cdot COOH$ (Fittig and Zanner, *Abstr.*, 1890, 589), which was identified by its boiling point, and by its being converted into isoeptolactone when heated with dilute sulphuric acid; together with the isoeptenoic acid a small quantity of the *β-hydroxyisoeptenoic acid* of Fittig and Feurer (*Abstr.*, 1895, i, 206) was formed. Isoeptenoic acid, together with a small quantity of isoeptolactone, are formed when the nitrile is hydrolysed by concentrated hydrochloric acid.

By heating cyanacetic acid (1 mol.) with propaldehyde (1 mol.) in a

sealed tube at 85° during 4—5 hours, a small quantity of methyl-ethylacraldehyde is formed, together with a larger quantity of an unsaturated *ciano-acid*, $\text{CHEt}\cdot\text{C}(\text{CN})\cdot\text{COOH}$ or $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{CN})\cdot\text{COOH}$,

which crystallises from a mixture of ether and light petroleum in white plates, melts at $64\text{--}65^{\circ}$, and is easily soluble in water. When this is heated with 10 per cent. aqueous potash, ammonia is evolved and propaldehyde and malonic acid are formed; when heated alone above 100° , carbonic anhydride is evolved and a *pentenonitrile*, $\text{C}_5\text{H}_7\text{N}$, obtained, which boils at $147\text{--}150^{\circ}$, readily absorbs bromine, and dissolves with difficulty in water and carbon bisulphide, but easily in ether.

W. A. D.

Action of Sulphuric Acid on Elaidic Acid. By ALEX. TSCHERBAKOFF and ALEXANDER M. SAYTZEFF (*J. pr. Chem.*, 1898, [ii], 57, 27—35).—On adding sulphuric acid (sp. gr. = 1.80) gradually to melted elaidic acid at 50° , and subsequently decomposing with water the product obtained, a hydroxystearic acid is formed, which, from its properties, and those of its sodium, calcium, barium, zinc, and silver salts, appears to be identical with the acid obtained by similarly treating oleic acid (M. and A. Saytzeff, *Abstr.*, 1887, 30). When distilled, it is decomposed, like the latter acid (*Abstr.*, 1888, 815), into a mixture of oleic and isooleic acids. The configuration of the hydroxystearic acid is discussed.

W. A. D.

Preparation of Lactic Acid. By GEORG KASSNER (*Chem. Centr.*, 1897, ii, 20; from *Apoth. Zeit.*, 12, 325—326).—According to the author, lactic acid cannot well be prepared by adding zinc oxide to a fermenting solution of cane-sugar, partly inverted by the action of tartaric acid, as the oxide stops the fermentation and the original sugar is obtained. The following method is described. 300 grams of cane-sugar and 1.5 grams of tartaric acid are dissolved in 1700 grams of boiling water and the solution kept at 60° for several days. One hundred grams of old cheese mixed with water and a little more than the calculated quantity of calcium carbonate are then added and the fermentation allowed to proceed for about three weeks; after this time only about 21.5 grams of invert-sugar remain unattacked. The mixture is then boiled, and the zinc salt precipitated by adding zinc chloride to the filtrate. From this salt, the acid is obtained by the action of hydrogen sulphide.

E. W. W.

Racemism. By ALBERT LADENBURG [and in part W. HERZ] (*Ber.*, 1898, 31, 524—528).—The authors describe experiments which lead them to regard *i*-pyrotartaric acid as exhibiting partial racemism. Quinine *l*-pyrotartrate is more readily soluble than the *d*-salt.

It is held by the authors that racemic compounds exist in the liquid state, and that *i*-coniine is a racemic compound, because change of temperature occurs on mixing the *d*- and *l*-bases. Landolt's objection, that the same phenomenon attends admixture of ether and carbon bisulphide, is invalid, owing to the difference in density of these two substances.

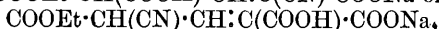
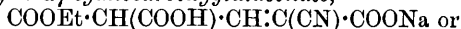
M. O. F.

Isomerides of Pyrocinchonic Acid. By ARTHUR H. E. KETTNER (*Chem. Centr.*, 1897, ii, 263—264; from *Diss. Strassburg*, 1897).—In contradiction to the statement of Delisle, the author has proved that pyrocinchonic acid or its anhydride, when warmed with sodium hydroxide, is converted into dimethylfumaric acid (β -methylmesaconic acid) and methylitaconic acid, a state of equilibrium being attained which varies with the concentration of the alkali employed. Dimethylfumaric acid is slightly soluble in cold water and melts at 239—240°. On dry distillation, it is partly converted into pyrocinchonic anhydride, the complete change being effected by the action of acetic chloride under pressure or of bromine in sunlight. The alkaline earth salts are easily soluble in water. The acid does not form an anhydride when boiled with sodium hydroxide, but yields the isomeric acids. Methylitaconic acid is easily soluble in water, melts at 150—151°, and forms slightly soluble alkaline earth salts; when boiled with sodium hydroxide, it is partly changed into the isomeric acids, and with bromine it forms a *dibromide*, $C_6H_8O_4Br_2$, melting at 153° but pyrocinchonic anhydride is not produced. When heated alone, it yields pyrocinchonic anhydride, but by the action of acetic chloride, *methylitaconic anhydride* is obtained; this crystallises from carbon bisulphide, melts at 62—63°, with water forms methylitaconic acid and on heating is converted into pyrocinchonic anhydride.

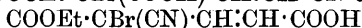
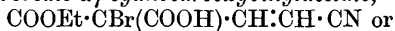
On reduction, all three isomeric acids yield the same symmetrical dimethylsuccinic acid. E. W. W.

Derivatives of Glutaconic Acid. By GIORGIO ERRERA (*Gazzetta*, 1897, 27, ii, 393—412).—Ethyllic cyanacetate reacts with chloroform and sodium ethoxide in a manner analogous to ethylic malonate and in accordance with the equation $2COOEt \cdot CH_2 \cdot CN + CHCl_3 + 4NaOEt = 3NaCl + 4EtOH + COOEt \cdot CNa(CN) \cdot CH : C(CN) \cdot COOEt$. The reaction proceeds rapidly on the water bath, and after a few minutes heating the product is poured into alcohol, the sodium chloride filtered off, and the filtrate evaporated; the *ethyllic sodio- α -dicyanoglutaconate* which separates on cooling is purified by crystallisation from alcohol. It crystallises in thin, colourless needles containing either alcohol or $2H_2O$, melts and decomposes at 265°, and is not decomposed by boiling with water. The corresponding *calcium* compound, $Ca(C_{11}H_{11}N_2O_4)_2 + 4H_2O$, crystallises in long, yellow needles. On treating a hot aqueous solution of the sodio-derivative with hydrochloric acid, *ethyllic α -dicyanoglutaconate*, $COOEt \cdot CH(CN) \cdot CH : C(CN) \cdot COOEt$, separates and is ultimately obtained in yellow laminae melting at 178—179°. It is accompanied by a white, crystalline compound, $C_{11}H_{16}N_2O_6$, which begins to decompose at 160° and is obtained by boiling the dicyanoglutaconate with alcohol; this probably has the constitution $COOEt \cdot CH(CN) \cdot CH : C(CONH_2) \cdot COOEt + H_2O$, and when heated in sulphuric acid solution or with soda yields *diethyllic α -cyanocarboxyglutaconate*, $COOEt \cdot CH(COOH) \cdot CH : C(CN) \cdot COOEt$ or $COOEt \cdot CH(CN) \cdot CH : C(COOH) \cdot COOEt$, which crystallises in colourless laminae melting at 191°, and forms a crystalline *sodium* salt, $C_{11}H_{12}NO_6Na + 2H_2O$.

Sodium ethylic α -cyanocarboxyglutaconate,



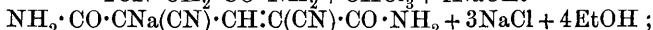
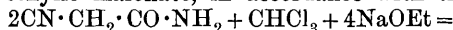
obtained by boiling diethylic cyanocarboxyglutaconate with aqueous soda, crystallises in small, colourless tablets containing $2\text{H}_2\text{O}$, and when treated with concentrated sulphuric acid and then with water, yields a crystalline precipitate of the corresponding *ethylic dihydrogen salt*. On boiling the liquid, however, carbonic anhydride is evolved and *ethylic α -cyanocarboxyvinylacetate*, $\text{COOEt} \cdot \text{CH}(\text{COOH}) \cdot \text{CH} : \text{CH} \cdot \text{CN}$ or $\text{COOEt} \cdot \text{CH}(\text{CN}) \cdot \text{CH} : \text{CH} \cdot \text{COOH}$, separates; this crystallises in hard prisms melting at 179° , and yields a crystalline *sodium salt*, $\text{C}_8\text{H}_8\text{NO}_4\text{Na}$. On adding bromine to a warm aqueous solution of the monethylic salt, *monethylic α -bromo- α -cyanocarboxyvinylacetate*,



is obtained; it crystallises in white needles.

On boiling monethylic cyanocarboxyvinylacetate with potash and subsequently adding hydrochloric acid, *γ -cyanovinylacetic acid*, $\text{CN} \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$, is obtained; it crystallises in yellow prisms melting at 185 — 195° and is possibly a γ -cyanocrotonic acid of the constitution $\text{CN} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{COOH}$. W. J. P.

Condensation of Cyanacetamide with Chloroform. By GIORGIO ERRERA (*Gazzetta*, 1897, 27, ii, 412—416).—Cyanacetamide reacts with chloroform and sodium ethoxide, in a manner analogous to ethylic malonate, in accordance with the equation:—



sodio- α -dicyanoglutaconamide, obtained thus, crystallises in yellow needles, and when treated with hydrochloric acid in aqueous solution yields *α -dicyanoglutaconamide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$, which crystallises in yellow laminæ melting and decomposing at above 280° and containing more than $1\text{H}_2\text{O}$.

On dissolving the amide in concentrated sulphuric acid, heating to 100° , and precipitating with water, the *amide of α -carboxy- γ -cyanoglutaconic acid*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CH} : \text{C}(\text{CO} \cdot \text{NH}_2)_2$, separates; it crystallises in yellow laminæ containing $\frac{1}{2}\text{H}_2\text{O}$. W. J. P.

Formation of Carbonic Oxide from Ethylic Oxalacetate and its Derivatives (IV.) and Ethylic Benzyloxalacetate. By WILHELM WISLICENUS and MAX MÜNZESHEIMER (*Ber.*, 1898, 31, 551—557).—When ethylic ethoxyoxalacetate, $\text{COOEt} \cdot \text{CO} \cdot \text{CH}(\text{OEt}) \cdot \text{COOEt}$, is heated in a stream of carbonic anhydride to a temperature of 180° , carbonic oxide is evolved, this evolution becoming much brisker as the temperature reaches 200° ; on raising the temperature, *ethylic ethoxymalonate* (b. p. 228°) distils over. When this salt is hydrolysed with the requisite quantity of sodium hydroxide solution, and then neutralised with the requisite quantity of dilute sulphuric acid, *ethoxymalonic acid* is obtained. This is best extracted with ether, and recrystallised from light petroleum (b. p. 35 — 50°) and ether; it forms colourless, glistening prisms, melts at 123 — 125° , is readily soluble in water or in ether, and

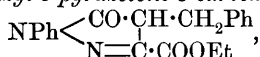
dissolves but sparingly in light petroleum or benzene. The *barium* and *silver* salts have also been prepared. When ethylic ethoxymalonate is warmed on the water bath with slightly less than the calculated quantity of phenylhydrazine, *phenylhydrazinomalononic acid dihydrazide*, $\text{N}_2\text{H}_2\text{Ph}\cdot\text{CH}(\text{CO}\cdot\text{N}_2\text{H}_2\text{Ph})_2$, is formed; this crystallises from glacial acetic acid in yellowish plates melting at $256-257^\circ$, and its solution in concentrated sulphuric acid gave a deep red coloration with ferric chloride or potassium dichromate.

When the ethylic salt is heated with aniline (3 mols.) on the water bath, the chief products are *ethoxymalonodianilide* and the *dianilide* of anilidomalonic acid. The latter compound is practically insoluble in hot alcohol, but crystallises from acetic acid in glistening plates, and melts at $246-247^\circ$. Conrad and Bischoff have previously (*Annalen*, 209, 231) described this compound as melting at 162° . The dianilide of ethoxymalononic acid is readily soluble in hot alcohol, from which it may be crystallised; it melts at $170-171^\circ$, and gives a reddish-violet colour with sulphuric acid and ferric chloride.

Ethylic ethoxymethylmalonate, $\text{OEt}\cdot\text{CMe}(\text{COOEt})_2$, is obtained when ethylic ethoxymalonate is treated with sodium, and then with methylic iodide; it distils at 110° under 16 mm. pressure.

Ethylic benzyloxalacetate, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{COOEt})\cdot\text{CO}\cdot\text{COOEt}$, obtained by combining ethylic phenylpropionate with ethylic oxalate in the usual manner (*Annalen*, 1888, 246, 315), is a colourless oil, and cannot be distilled, even under diminished pressure, without undergoing decomposition. Its *copper* derivative, obtained by the action of copper acetate on an alcoholic solution of the ethylic salt, crystallises from hot alcohol in green needles, and melts at $136-138^\circ$. When heated to 200° , the ethylic salt loses carbonic oxide, and yields ethylic benzymalonate, and when hydrolysed with six times its weight of normal sulphuric acid, it yields *benzylpyruvic acid*, melting at $48-50^\circ$. The *hydrazone* of this acid crystallises from dilute alcohol in yellowish crystals melting at $149-151^\circ$; and when boiled with 10 per cent. alcoholic sulphuric acid yields *benzylindolecarboxylate*, which, after recrystallisation from a mixture of benzene and light petroleum, melts at $144-146^\circ$.

Ethylic 1-phenyl-4-benzyl-5-pyrazolone-3-carboxylate,



is obtained when ethylic benzyloxalacetate is warmed with the calculated quantity of phenylhydrazine for an hour on the water bath; it crystallises from alcohol in glistening needles, melts at 194° , and gives no coloration with sulphuric acid or ferric chloride. The mother liquor from this compound yields, on the addition of water, the *phenylhydrazone* of ethylic benzyloxalacetate melting at $64-66^\circ$.

Ethylic phthalideoxalate (*Annalen*, 1888, 246, 343), when heated, does not lose carbonic oxide. J. J. S.

Racemic Transformation of Hydrogen Ammonium Malate. By JACOBUS H. VAN'T HOFF and H. M. DAWSON (*Ber.*, 1898, 31, 528-534. Compare Kenrick, *Abstr.*, 1897, i, 506).—The statement is made by Pasteur that, on evaporating a solution of inactive hydrogen

ammonium malate, a substance first separates having the form and composition of the active salt without exhibiting hemihedral faces; this is followed by the hydrated racemate investigated by Kenrick (*loc. cit.*).

Recognising that the former substance might be a pseudoracemic compound, according to the classification of Kipping and Pope (*Trans.*, 1897, 71, 989), the authors have examined it from this point of view. The result of their experiments shows that the substance in question is a mixture of 3 parts of *l*-malate with 1 part of the *d*-salt.

A mixture of *d*- and *l*-salts is more readily soluble than either of the active compounds alone; the racemate, in the stable form, is less soluble than either of the active salts, but at the temperature of transformation (76°) it is more readily soluble than the mixture.

M. O. F.

Action of Formaldehyde on Uric Acid. By K. WEBER and BERNHARD TOLLENS (*Annalen*, 1898, 299, 340—346).—Uric acid combines with formaldehyde, yielding (1) a crystalline, sparingly soluble compound, $C_7H_8N_4O_5$, containing two molecular proportions of formaldehyde, and (2) an amorphous, very readily soluble compound, which contains four or five molecular proportions of formaldehyde. The crystalline derivative forms barium and calcium salts, which separate initially as white precipitates, and become gelatinous on agitation.

M. O. F.

Condensations of Furfuraldehyde and Furfuracraldehyde. By H. RÖHMER (*Ber.*, 1898, 31, 281—285).—The condensations were effected by heating the two substances together with acetic anhydride or glacial acetic acid, and then either pouring the product into water and extracting with ether, or adding soda, decomposing the sodium salt with sulphuric acid, and then extracting with ether. With pyruvic acid, furfuraldehyde forms yellow *furfurylidenepyruvic acid*, $C_4OH_3 \cdot CH:CH \cdot CO \cdot COOH$, which melts at 110°, and, when heated at 100° with alcohol, yields a yellow *ethylic* salt melting at 44—45°. With sodium phenylacetate, furfuraldehyde forms *furfurylidenephnylacetic acid*, $C_4OH_3 \cdot CH:CH \cdot CPh \cdot COOH$; this melts at 143—144°, and, by mixing it with phosphoric chloride and treating the product with piperidine in benzene solution, it can be made to yield a *piperidide*, melting at 105°.

Furfuracraldehyde condenses with acetone in aqueous solution in the presence of a little soda; the yellow product, *furfuracrylideneacetone*, $C_4OH_3 \cdot CH:CH \cdot CH:CH \cdot CMeO$, melts at 33—34°, and its yellowish *oxime* at 122—123°; with acetophenone, it condenses to yellow *furfuracrylideneacetophenone*, $C_4OH_3 \cdot CH:CH \cdot CH:CH \cdot CPhO$; this melts at 52—53°, and its *semicarbazide* at 59—60°; with sodium acetate, it condenses to the yellowish *furfuracrylideneacetic acid*,

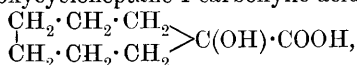
$C_4OH_3 \cdot CH:CH \cdot CH:CH \cdot COOH$, melting at 153—154°; with sodium phenylacetate, to yellow *furfuracrylidenephenylacetic acid*, $C_4OH_3 \cdot CH:CH \cdot CH:CH \cdot CPh \cdot COOH$, melting at 212—213°; with pyruvic acid, to yellowish *furfuracrylidenepyruvic acid*, which has no well-defined melting point; and with ethylic malonate to *ethylic furfuracrylidenemalonate*, which boils at 210—211° under

33 mm. pressure. The *semicarbazide* of *furfuracraldehyde* is yellow and melts at 215—219°. C. F. B.

Para- ψ -propylnaphthenic Acid (Hexahydrocuminic Acid). By WLADIMIR B. MARKOWNIKOFF (*J. pr. Chem.*, 1898, [ii], 57, 95—103).—*Hexahydrocuminic acid*, $C_{10}H_{18}O_2$, prepared by the action of sodium on cuminic acid in boiling amylic alcohol solution, forms monoclinic crystals melting at 94·5—95°. It is not readily volatile with steam, is almost insoluble in cold, more soluble in hot water, and readily so in benzene, chloroform, and ether. When heated to its boiling point (269°) for 2 hours, it is converted into an oily isomeride, which is still under investigation.

The *sodium*, *calcium*, *barium*, and *silver* salts are described. The *methylic* salt is a liquid boiling at 234—235°, of sp. gr. = 0·9614 at 0°/0°; the *amide*, which is produced on heating the methylic salt with concentrated ammonia for 20 hours at 100°, forms needle-shaped crystals melting at 169·5—170·5°. The *anilide* crystallises in needles melting at 204—205°. A. W. C.

Derivatives of Cycloheptane. By EDUARD BUCHNER and ANDREAS JACOBI (*Ber.*, 1898, 31, 399—402. Compare Abstr., 1897, i, 612).—The following salts of hydroxysuberanecarboxylic acid (suberylglucolic acid, 1-hydroxycycloheptane-1-carboxylic acid,

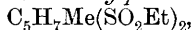


have been prepared:—*sodium*, with $2H_2O$; *calcium* and *barium*, each with $6H_2O$; *lead*, with $\frac{1}{2}H_2O$, and the anhydrous *silver* salt. The acid itself yields paratoluic acid when heated with strong sulphuric acid; when heated at 120—125° with strong hydrochloric acid, it yields chlorosuberanecarboxylic acid, and this, on boiling with alcoholic potash, yields suberenecarboxylic (Δ^1 -cycloheptenecarboxylic) acid. This has a striking similarity to the Δ^1 -1-ethylcyclopentene-4-carboxylic acid of Einhorn and Willstätter (Abstr., 1894, i, 524); its *amide*, however, melts at 125—126°. It has the character of an unsaturated compound; it decolorises permanganate at once in alkaline solution, and is reduced by sodium in boiling amylic alcohol solution to suburanecarboxylic (cycloheptanecarboxylic) acid, an oil which yields pimelic acid when oxidised, and of which the *amide* melts at 193—194°, almost the melting point of 1-ethylcyclopentane-4-carboxylamide.

C. F. B.

Sulphonals of Cyclic Ketones. By OTTO WALLACH and WALTHER BORSCHÉ (*Ber.*, 1898, 31, 338—339).—Cyclic ketones yield sulphonal derivatives which are strictly analogous to those derived from acetone.

Pentanonesulphonal, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{SO}_2\text{Et})_2$, is prepared by acting on pentanone and ethylic mercaptan with hydrogen chloride, and treating the product with potassium permanganate solution; it separates from hot water in feathery crystals, and from alcohol in thin, nacreous plates melting at 127—128°. *Methylpentanonesulphonal*,



crystallises from dilute methylic alcohol in lustrous, oblique prisms

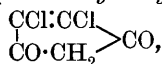
melting at 110.5—111.5°. *Methylhexanonesulphonal* is sparingly soluble in cold water and melts at 104—105°, whilst *heptanonesulphonal*, prepared from suberone, crystallises from alcohol in compact prisms melting at 136—138°. A. H.

Action of Ammonia on Hexachloroketo-R-pentene (m. p. 28°). By E. C. THEODOR ZINCKE and ALBERT ROHDE (*Annalen*, 1898, 299, 367—382).—*Amidopentachloroketo-R-pentene*,
$$\begin{array}{c} \text{CCl} \text{---} \text{CCl}_2 \\ | \\ \text{C}(\text{NH}_2) \cdot \text{CCl}_2 \end{array} > \text{CO},$$

or $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{CCl}_2 \cdot \text{CCl}_2 \\ || \\ \text{CCl} \end{array} > \text{CO}$, is prepared by dissolving the hexachloroketo-R-pentene which melts at 28° (Abstr., 1897, i, 507) in benzene, and saturating the ice cold solution with dry ammonia; it crystallises from hot benzene in colourless, rhombic leaflets, and melts at 118°. When crystallised from hot water, or from hot dilute hydrochloric or nitric acid, it forms long, colourless needles, and melts at 127°, but recrystallisation from benzene depresses the melting point to 118°. The compound is indifferent towards hydrochloric, nitric, nitrous, and concentrated sulphuric acids, acetic anhydride, and phosphorus pentachloride; it dissolves in alkalis, and the liquid becomes brown when heated, the odour of isonitrile becoming perceptible.

Amidoheptachloroketo-R-pentane,
$$\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{CCl}_2 \cdot \text{CCl}_2 \\ || \\ \text{CCl} \text{---} \text{CCl}_2 \end{array} > \text{CO},$$
 obtained by dissolving the foregoing substance in glacial acetic acid, and saturating the liquid with chlorine, forms lustrous, prismatic crystals, melts at 72°, and boils at 165° under a pressure of 30—33 mm. It is insoluble in cold, aqueous alkali, and is but slowly attacked by the hot liquid; hot concentrated sulphuric acid has no action on the substance.

Dichlorodiketo-R-pentene (dichlorohydroxyketo-R-pentinene),



or $\text{CCl} : \text{CCl} \begin{array}{c} \diagup \\ \text{C} \cdot \text{OH} \end{array}$, is prepared by the action of stannous chloride on the foregoing ketones; it crystallises from benzene in monoclinic plates and melts at 162°. The substance sublimes in large, lustrous leaflets, and is volatile in an atmosphere of steam; the vapour has an irritating effect on the mucous membrane.

Hexachlorometadiketo-R-pentane,
$$\begin{array}{c} \text{CCl}_2 \cdot \text{CCl}_2 \\ | \\ \text{CO} \text{---} \text{CCl}_2 \end{array} > \text{CO},$$
 is produced by the action of chlorine on dichloroketo-R-pentene dissolved in glacial acetic acid. It separates from the dilute acid in thick, colourless crystals and melts at 70°; it is readily volatile, and the odour suggests camphor and quinone. Caustic soda converts the substance into trichloracrylic acid, and ammonia gives rise to the *amide* of dichloracetyltetrachloropropionic acid, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{CCl}_2 \cdot \text{CCl}_2 \cdot \text{CO} \cdot \text{NH}_2$, which crystallises from benzene in slender, colourless needles, and melts at 155—156°; reduction with stannous chloride converts this compound into the amide of dichloracetyldichloracrylic acid.

M. O. F.

Preparation of Diorthonitrotoluene. By ARNOLD F. HOLLEMAN and J. BOESEKEN (*Rec. Trav. Chim.*, 1897, **16**, 425—428).—A 20 per cent. yield of dinitroparatoluidine [$\text{Me}:(\text{NO}_2)_2:\text{NH}_2 = 1:2:6:4$] may be obtained from sym.-trinitrotoluene as follows. Fifty grams of trinitrotoluene are triturated with 100 c.c. of alcohol (95 per cent.), and the mixture is slowly added, with constant stirring, to 60—70 c.c. of ammonium hydrosulphide solution (prepared by saturating a 20 per cent. solution of ammonia with hydrogen sulphide). The mixture is immersed in cold water if necessary. The reaction is ended when the liquid only slowly darkens lead acetate paper. The mixture is then evaporated just to dryness on the water bath, and the dinitrotoluidine extracted with boiling hydrochloric acid (sp. gr. = 1.055). After precipitation with ammonia and recrystallisation from 40 per cent. acetic acid, it forms yellowish-red needles melting at 171° . A small quantity (some 2 grams from 200 of trinitrotoluene) of the isomeric *dinitrotoluidine* [$\text{Me}:(\text{NO}_2)_2:\text{NH}_2 = 1:4:6:2$] may be extracted from the mother liquor after recrystallisation from dilute acetic acid; it melts at 155° . The amido-group can readily be removed from both dinitrotoluidines by the following method. One gram of the nitrated toluidine is dissolved in 10 c.c. of concentrated sulphuric acid, and the solution diluted with its own volume of water, care being taken to keep the mixture cold. The requisite quantity of sodium nitrite, dissolved in the smallest possible quantity of water, is run into the ice cold solution, which is then poured as quickly as possible into 25 c.c. of boiling alcohol (96 per cent.); after the evolution of gas has ceased, the mixture is poured into water and the dinitrotoluene can be collected. Diorthonitrotoluene after recrystallisation from light petroleum melts at 66° (not $60\text{--}61^\circ$). It has not been found possible to replace any of the hydrogen atoms of the methyl groups in either 2:6-dinitro- or 2:4:6-trinitro-toluene by chlorine. The authors attribute this to the protective influence of the nitro-groups in the ortho-positions. J. J. S.

Phenylethylallylcarbinol. By ALEXIS BOGORODSKY and J. LJUBARSKY (*J. pr. Chem.*, 1898, [ii], **57**, 44—48).—*Phenylethylallylcarbinol*, prepared by leaving phenyl ethyl ketone (1 mol.) and allylic iodide (2 mols.) in contact with zinc turnings during a week, and subsequently decomposing with water, the additive product formed is a mobile, highly refractive liquid, which has a slightly aromatic odour, is insoluble in water, and boils at $238\text{--}242^\circ$; on oxidation with aqueous potassium permanganate, it yields a trihydric alcohol, $\text{OH}\cdot\text{CetPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$. This is a thick, yellow syrup, which appears to be converted by acetic anhydride into a mixture of its triacetate, and the diacetate of a glycol, $\text{CetPh}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ (compare this vol., i, 291). W. A. D.

Action of Chlorine on Quinones and Quinoneoximes. By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1897, **27**, ii, 572—587).—Whilst quinone yields a tetrachloride or tetrabromide, substituted quinones do not form additive compounds with more than 2 atoms of halogen.

On treating nitroso-orthocresol in chloroform solution with chlorine in the cold, driving off the chloroform by a current of car-

bonic anhydride, allowing the residue to stand, and crystallising from chloroform, a *nitroso-orthocresol dichloride* of the constitution $\text{CO} \begin{array}{c} \text{CHCl} \cdot \text{CHCl} \\ \text{CMe} = \text{CH} \end{array} \text{C} \cdot \text{N} \cdot \text{OH}$ is obtained, crystallising in colourless prisms, and melting at $153-154^\circ$ with decomposition. When heated with aqueous alcohol, it yields a *chloronitrosocresol*, $\text{C}_7\text{H}_6\text{NO}_2\text{Cl}$, which crystallises in yellow needles melting and decomposing at $158-159^\circ$, and gives Liebermann's nitroso-reaction.

Nitrosometacresol, when similarly treated with chlorine, yields an α -*toluquinoneoxime dichloride*, $\text{CO} \begin{array}{c} \text{CHCl} \cdot \text{CHCl} \\ \text{CH} = \text{CMe} \end{array} \text{C} \cdot \text{N} \cdot \text{OH}$, which crystallises in colourless prisms melting and decomposing at $150-152^\circ$; on heating with aqueous alcohol, it yields a *chloronitrosocresol*, $\text{C}_7\text{H}_6\text{NO}_2\text{Cl}$, which crystallises in colourless needles melting and decomposing at $147-148^\circ$, and resembles its ortho-isomeride in general properties.

Nitrosothymol, on treatment with chlorine in chloroform solution, yields a *chloronitrosothymol*, $\text{C}_{10}\text{H}_{12}\text{NO}_2\text{Cl}$, which crystallises in yellow needles melting at $162-163^\circ$ with decomposition, and gives Liebermann's reaction. Nitrosocarvacrol, under similar conditions, yields a *chloro-derivative*, $\text{C}_{10}\text{H}_{12}\text{NO}_2\text{Cl}$, which crystallises in yellow needles melting and decomposing at $157-158^\circ$. Thymoquinone, on treatment with chlorine, yields a mixture of mono- and dichloro-thymoquinones which could not be satisfactorily separated. Orthodichloroquinone, when treated with chlorine as above, yields only chloranil, whilst the meta- and para-isomerides are not acted on by chlorine. W. J. P.

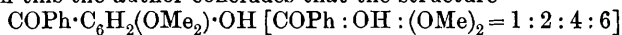
A New Synthesis of Phloroglucinol. By E. FLESCHE (*Monatsh.*, 1897, 18, 755-763).—Since phloroglucinol, as usually prepared, is always contaminated with diresorcinol, the author recommends the following method of preparation. Picric acid is first converted into picryl chloride, which is then reduced by tin and hydrochloric acid to symmetrical triamidobenzene; on heating the hydrochloride of the latter (50 grams), in an atmosphere of hydrogen during 8 hours, with water (2-5 litres) from which air has been expelled by boiling, an 80-90 per cent. yield of pure phloroglucinol is obtained (compare Pollak, Abstr., 1894, i, 22).

The symmetrical *triacetamidobenzene* crystallises from alcohol in white rhombic plates, melts at 208° (uncorr.), and is easily soluble in boiling water but insoluble in ether and benzene. W. A. D.

Ethers of Phloroglucinol and a Synthesis of Hydrocotoin. By J. POLLAK (*Monatsh.*, 1897, 18, 736-748).—Phloroglucinol dimethylic ether, prepared by Will's method (Abstr., 1888, 457), is easily soluble in most solvents, but separates from its benzene solution on adding light petroleum in colourless crystals which melt at $36-38^\circ$ (uncorr.); its *benzoyl* derivative, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{OBz}$, is very soluble in the ordinary solvents, but crystallises from light petroleum or dilute alcohol in slender, glistening needles, and melts at $41-43^\circ$ (uncorr.). On heating the latter compound with benzoic chloride and zinc chloride (compare Ciamician and Silber, Abstr., 1894, i, 409), the benzoyl derivative of hydrocotoin is formed, which melts at $117-118^\circ$ (uncorr.),

and not at 113° as stated by Hesse (Abstr., 1895, i, 110); it separates from a concentrated alcoholic solution in needles, but when the latter is dilute, in thin, lustrous plates. When boiled with alcoholic potash, it is converted into hydrocotoin; if the latter is heated with acetic anhydride and sodium acetate, there is formed, together with the acetate (compare Hesse, *Annalen*, 190, 60), a small quantity of *meta*-dimethoxy- β -phenylcoumarin, $C_6H_2(OMe)_2$ $\begin{matrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \text{---} \text{CO} \\ \diagdown \quad \diagup \\ \text{CPh} \text{:CH} \end{matrix}$, which crystallises from alcohol in silky needles, melts at $166\text{--}167^{\circ}$ (uncorr.), and is converted by concentrated hydriodic acid into Kostanecki and Weber's metadihydroxy- β -phenylcoumarin (Abstr., 1894, i, 88).

From this the author concludes that the structure



must be attributed to hydrocotoin (compare Ciamician and Silber, Abstr., 1894, i, 255).

Phloroglucinol monethylic ether (this vol., i, 16) boils at $220\text{--}221^{\circ}$ (uncorr.) under 30 mm. pressure, does not yield an oxime, and is converted into phloroglucinol diethylic ether by passing hydrogen chloride through its alcoholic solution; when, however, it is heated with ethylic iodide and potash, a viscous oil is obtained, which is probably a mixture of "pseudo-ethers" (compare Herzig and Zeisel, Abstr., 1888, i, 822).

The *diacetyl* derivative of phloroglucinol monethylic ether crystallises from light petroleum in small, colourless plates, and melts at $40\text{--}42^{\circ}$ (uncorr.); the *dibenzoyl* derivative is moderately soluble in alcohol, ether, and benzene, and crystallises from light petroleum in colourless plates which melt at $75\text{--}77^{\circ}$ (uncorr.). W. A. D.

Action of Ortho-xylylenic Bromide on Primary, Secondary, and Tertiary Amines. By MAX SCHOLTZ (*Ber.*, 1898, 31, 414—431).—Ortho-xylylenic bromide, $C_6H_4(CH_2Br)_2$, reacts with aniline in chloroform solution at the ordinary temperature, forming *2'-phenyl-dihydroisoindole*, $C_6H_4:(CH_2)_2:NPh$, which melts at 165° , and has no basic properties; in the same way, *meta*- and *para*-tolyl- and *paramisyl-dihydroisoindoles*, melting at 115° , 195° , and 214° respectively were prepared. With benzylamine, the reaction takes place even more readily, and the product, *2'-benzyl-dihydroisoindole*, melts as low as 41° , and has basic properties, dissolving in dilute hydrochloric acid and forming a *hydrochloride* which melts at 198° . With amines containing CH_3 or other groups in the ortho-position relatively to the NH_2 group, no such ring-formation takes place; orthotoluidine, xylydine [$Me_2:NH_2 = 1:3:4$], and pseudocumidine yield respectively *xylyleneditoluidine*, *xylyleneditoxylydine*, and *xylylenedipseudocumidine*, $C_6H_4(CH_2 \cdot NHR)_2$, melting at 148° , 106° , and ? (not stated), whilst orthanisidine and α -naphthylamine yield compounds of the type $CH_2Br \cdot C_6H_4 \cdot CH_2 \cdot NHR$; that formed in the last case melts at $240\text{--}242^{\circ}$.

With secondary amines, NHR'_2 , or $NH \cdot R''$, ortho-xylylenic bromide forms substituted ammonium bromides of the type $C_6H_4:(CH_2)_2:NR'_2Br$ or $C_6H_4:(CH_2)_2:NBr \cdot R''$, and these react with a molecule of the same or another amine at 200° , and in aqueous or alcoholic solution, yielding diacid bases of the type $C_6H_4(CH_2 \cdot NR'_2)_2$ or $NR'_2 \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot N \cdot R''$. *Xylylenediethylammonium bromide* is a syrup, the *aurochloride* melts at

124°, and the *platinochloride* at 225°; *xylylene-di-diethylamine* boils at 170—175° under 20 mm. pressure. *Xylylene-di-isobutylammonium bromide* melts at 273°, the *aurochloride* at 129°, and the *platinochloride* at 208°; *xylylene-di-di-isobutylamine* melts at 56°, and boils above 200° under 20 mm. pressure. *Xylylenepiperidonium bromide* melts at 234° and the *aurochloride* at 130°, the *platinochloride* decomposes above 230°, and the *periodide*, $C_6H_4:(CH_2)_2:NC_5H_{10}I_5$ at 92°; *xylylenedipiperidyl* boils at 190—195° under 20 mm. pressure, the *aurochloride* melts at 204°, the *platinochloride* melts and decomposes at 240°, and the *dimethiodide* melts at 234°; *xylylenepiperidyl-diethylamine* boils at 175—180° under 20 mm. pressure, its *dimethiodide* melts at 216°; *xylylenepiperidyl-di-isobutylamine* boils at 196—198° under 20 mm. pressure. With secondary amines in which at least one tertiary carbon atom is directly connected with the NH_2 group, a compound of the type $C_6H_4(CH_2 \cdot NR'_2)$ is formed at once, even at the ordinary temperature; monomethylaniline yields *xylylene-di-phenylmethylamine*, melting at 110°, and diphenylamine, although less readily, *xylylene-di-diphenylamine*, melting at 179°.

With tertiary amines, ortho-xylylenic bromide forms substituted diammonium bromides, $C_6H_4(CH_2 \cdot NR'''Br)_2$. With pyridine, *xylylene-di-pyridonium bromide* is obtained, melting at 134°, the orange *per-bromide* of which, $C_6H_4(CH_2 \cdot NC_5H_5Br)_2Br_4$, melts at 141°; the *aurochloride* melts at 240°, the *platinochloride* at 245—246°. Tri-propylamine appears to react in a similar manner.

Attention is called to the fact that, in the reaction between ortho-xylylenic bromide and a primary amine, formation of a ring-compound (dihydroisindole) is prevented by the presence, in one only of the two ortho-positions relatively to the NH_2 group, of methyl (in toluidine, xylidine, and pseudocumidine), OCH_3 (in anisidine), or a second benzene ring (in naphthylamine); presence of phenylic hydrogen in the ortho-position (as in aniline) is, moreover, less favourable to the reaction than that of methylenic hydrogen (as in benzylamine). In the reaction with secondary amines, the formation of a ring-compound (substituted ammonium bromide) is prevented when the NH_2 group is attached even to one tertiary carbon atom, and when it is attached to two of these, even such reaction as does occur takes place yet less readily.

C. F. B.

Oxidation of Orthethylamidophenol. By EMIL DIEFOLDER (*Ber.*, 1898, 31, 495—500).—Orthethylamidophenol, $OH \cdot C_6H_4 \cdot NHEt$, was prepared by heating orthanisidine, $OMe \cdot C_6H_4 \cdot NH_2$, with ethylic bromide for 5 hours at 59°, treating the product with nitrous acid, separating the orthethylanisidinenitrosamine, and converting it into orthethylanisidine, $OMe \cdot C_6H_4 \cdot NHEt$ (which boils at 117° under 3 mm. pressure, at 228—229° (uncorr.), under 728 mm.; the hydrochloride melts at 193°); from this, the methyl group was eliminated by heating with fuming hydrochloric acid for 4 hours at 170°.

When orthethylamidophenol is dissolved in twenty times its weight of $12\frac{1}{2}$ per cent. sulphuric acid, and 120—130 c.c. of 10 per cent. sodium dichromate solution (containing $4H_2SO_4$) is gradually added while the mixture is continually shaken, and it is then extracted with

chloroform, the filtered chloroform extract, on concentration, yields *N*-ethylphenoxazineorthoquinone, $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown NEt \end{smallmatrix} \begin{smallmatrix} \diagdown C:CH \cdot CO \\ \diagup C:CH \cdot CO \end{smallmatrix}$, in dark-red crystals, with a green, metallic reflex, and melting at 226° ; ethylamine is also formed, and the reaction takes place according to the equation $2C_8H_{11}NO + 3O = C_{14}H_{11}NO_3 + NH_3Et + 2H_2O$. The quinone is reduced, and at the same time acetylated, by zinc dust and acetic anhydride, and *diorthacetox-N*-ethylphenoxazine, $C_{14}H_{11}NO(OAc)_2$, melting at 110° is formed. Further, it dissolves in sodium hydrogen sulphite solution, and yields a yellow *dioxime* which decomposes at 140° and crystallises with $1\frac{1}{2}H_2O$, and a red *mono-semicarbazone* which melts and decomposes at 243° . When it is warmed with orthophenylenediamine in acetic acid solution, and the acetate which separates is decomposed by boiling with alcohol, orange *N*-ethyltriphenoxazine, $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown NEt \end{smallmatrix} \begin{smallmatrix} \diagdown C_6H_4 \\ \diagup C_6H_4 \end{smallmatrix} \begin{smallmatrix} \diagup N \\ \diagdown N \end{smallmatrix} C_6H_4$, melting at 229° , is obtained. It also reacts with phenylhydrazine, yielding a violet-brown substance, with greenish lustre, which melts at 210 – 211° . C. F. B.

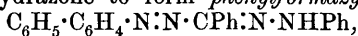
Diazonium Hydroxide in Aqueous Solution. By ARTHUR HANTZSCH (*Ber.*, 1898, 31, 340–348).—When pure diazonium chloride is dissolved in water at 0° and treated with a small excess of freshly precipitated silver oxide, a solution of diazonium hydroxide is obtained, free from chlorine and silver, which contains 70–75 per cent. of the calculated amount of the hydroxide, the remainder being present in the residue in the form of silver diazotate. A solution of the hydroxide can also be obtained by treating a solution of diazonium sulphate with the calculated amount of aqueous barium hydroxide, as much as 96 per cent. of the calculated amount of hydroxide being thus obtained in solution when a $\frac{1}{40}$ – $\frac{1}{50}$ normal solution of the sulphate is employed. The solutions are colourless when pure, but usually have a faint yellowish tint, and are strongly alkaline, so that they can be readily titrated with acid, methyl-orange being the best indicator. They cannot be preserved for long, since they gradually decompose even in the cold, more rapidly on warming, into phenol and nitrogen, a considerable amount of a resinous diazo-compound being also formed; this yields nitrogen when heated with dilute acids. The solutions are also readily decomposed by animal charcoal, copper powder, alcohol and hydrogen sulphide. Silver nitrate and mercuric chloride produce heavy precipitates, whilst cobalt salts are decolorised. The hydroxide readily forms colouring matters with aqueous and alkaline solutions of α - and β -naphthol, resorcinol, and phloroglucinol, less readily with phenol, or paracresol; catechol and pyrogallol yield colouring matters, but a certain amount of nitrogen is evolved, whilst quinol causes a vigorous evolution of nitrogen but produces no colouring matter. Ammonia gives a deep orange coloration, probably due to the formation of bisdiazamidobenzene, whilst with aniline, bisdiazobenzeneanilide, $Ph \cdot N_2 \cdot NPh \cdot N_2 \cdot Ph$, exploding at 80 – 81° is obtained. Zinc dust converts the hydroxide into phenylhydrazine, the same effect being more slowly produced by sulphurous acid, a diazonium sulphite being probably first formed. The diazonium hydroxides of methyl derivatives

of diazonium chloride are much less stable, whilst it was found impossible to obtain an analogous compound from naphthylamine. The hydroxides derived from halogen substituted bases are, however, more stable but can only be obtained in very dilute solution, because they very readily yield insoluble diazo-oxides or metallic diazotates.

It will be proved in a future communication that diazonium hydroxide is a stronger base than ammonia, and that pure diazobenzene sodium is partially hydrolysed in dilute solution, with formation of the hydroxide, whilst the presence of soda prevents this action; this accounts for the fact observed by Bamberger, who found that the diazotates and isodiazotates, on reduction, behave differently towards phenylhydrazine in dilute solution and in the absence of an excess of alkali. When an excess of alkali is present, under which conditions no hydrolysis occurs, the two compounds behave in a precisely similar manner with phenylhydrazine, both as regards reduction and reaction.

A. H.

The Replacement of one of the Diazo-groups in Diphenyl-tetrazochloride by Hydrogen. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 479—483).—When an alcoholic solution of diphenyltetrazochloride, prepared by diazotising benzidine in alcoholic solution, is mixed with an alcoholic solution of benzylidenehydrazone in presence of alcoholic potash, one of the diazo-groups is replaced by hydrogen, and the paradiphenyldiazonium chloride, $C_6H_5 \cdot C_6H_4 \cdot N \cdot N \cdot Cl$, thus formed reacts with the hydrazone to form *phenylformazylbenzene*,

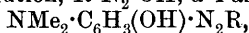


which is a dark violet powder, melts at 174° , and is converted by oxidation with nitrous acid in chloroform solution into tetraphenyl-tetrazolium chloride. A small quantity of diformazylbenzene is also formed, but this has not yet been obtained quite pure, and will form the subject of a future communication.

A similar reaction occurs when the alcoholic tetrazo-solution prepared from benzidine is treated with an alkaline solution of phenol, the product being *paraphenylhydroxyazobenzene*, $C_6H_5 \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot OH$, a brown, microcrystalline powder which melts at about 300° .

A. H.

New Primary Disazo-Dyes of the Benzene Series. By CARL BÜLOW and HANS WOLFS (*Ber.*, 1898, 31, 488—494).—When dimethylamidophenol [$NMe_2 \cdot OH = 1 : 3$], in cooled, dilute acetic acid solution is treated with a diazo-solution, $R \cdot N_2 \cdot OH$, a 4-azo-dye,



is formed; some new compounds of this class are described. When such a compound, in alkaline alcoholic solution at 0° , is treated with another diazo-solution, $R' \cdot N_2 \cdot OH$, the mixture being stirred for some time and then acidified with acetic acid, or saturated with carbonic anhydride, a 4 : 6-disazo-dye, $NMe_2 \cdot C_6H_2(OH)(N_2R) \cdot N_2R'$, is formed; several such compounds are described.

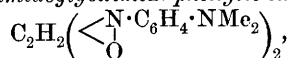
The new compounds described are tabulated below; under 4 and 6 are given the radicles, R and R' respectively, joined to those positions by the $\cdot N_2$ group; the 1 and 3 positions are occupied in all cases by NMe_2 and OH respectively. R and R' always contain a benzene

nucleus, and the position of substituting groups in this, relative to the $\cdot\text{N}_2\cdot$ group, is indicated by the accented numbers. Many of the substances have a greenish surface lustre in addition to the colour mentioned.

4.	6.	Colour.	Melting point.
2'-C ₆ H ₄ Me		Dark red	125—127°
4'-C ₆ H ₄ Me		Red	169—170
2' : 4'-C ₆ H ₃ Me ₂		Brownish-red	166—168
Ph	Ph	Brownish-black	136
Ph	2'-C ₆ H ₄ Me	Reddish-brown	139—140
2'-C ₆ H ₄ Me	Ph	Brown	124
Ph	4'-C ₆ H ₄ Me	Dark red	149
4'-C ₆ H ₄ Me	Ph	Brownish-black	143—144
Ph	2' : 4'-C ₆ H ₃ Me ₂	Brown	142
2' : 4'-C ₆ H ₃ Me ₂	Ph	Dark coloured	161

C. F. B.

Action of Diazomethane on Aromatic Nitro-Bases. By HANS VON PECHMANN and WILHELM SCHMITZ (*Ber.*, 1898, 31, 293—296).—By treating an ethereal solution of diazomethane with nitrosodimethylaniline, *tetramethyldiamidoglyoxime N-phenylic ether*,



is obtained, and can be purified by crystallisation from chloroform; it is red, and melts and decomposes at 245°. Hydrochloric acid of 20 per cent. strength decomposes it into glyoxal, nitrosodimethylaniline, and amidodimethylaniline; nitrosodimethylaniline hydrochloride crystallises out, and the filtrate, when rendered alkaline, deposits *tetramethyldiamidoglyoxaldianil*, $\text{C}_2\text{H}_2(\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, which is yellowish-brown, and melts at 256—257°. Boiling with phenylhydrazine and alcohol, and subsequent addition of acetic acid causes the ether to yield glyoxalosazone. Boiling with alcoholic potash converts it into parazoxydimethylaniline. Zinc and acetic acid reduce it in the cold to paramidodimethylaniline, and warming with chromic anhydride, oxidises it to quinone. *Tetremethyldiamidoglyoxime N-phenylic ether* is prepared in the same way as the methyl compound; it is red, and melts at 204°.

With diazomethane, nitrosoaniline yields red *diamidoglyoxime N-phenylic ether*, melting at 208°.

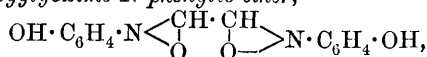
Metahydroxyparanitrosodiethylaniline yields dark-green *tetremethyl-diamidodimetahydroxyglyoxime N-phenylic ether*, which melts at 168°.

C. F. B.

Action of Diazomethane and of Methylic Iodide and Potash on Nitrosophenol. By HANS VON PECHMANN and EUGEN SEEL (*Ber.*, 1898, 31, 296—299).—The action of diazomethane on nitrosophenol gives rise to quinoneoxime methylic ether and paradihydroxyglyoxime N-phenylic ether; the latter is identical with the compound crystallising

in red needles obtained by the action of methylic iodide and potash, by ter Meer, and subsequently by Bridge.

Paradihydroxyglyoxime N-phenylic ether,



is insoluble in water and in common organic solvents; the solution in phenol is red, and deposits the substance in red needles when treated with alcohol and ether. It is insoluble in dilute acids, but forms a red solution in caustic soda and ammonia. The substance darkens at 210°, and decomposes at 250°. When boiled with alcohol, phenylhydrazine, and a small quantity of dilute acetic acid, the ether yields glyxalosazone. M. O. F.

Action of Diazomethane on Substituted Nitrosobenzenes.

By HANS VON PECHMANN and AUGUST NOLD (*Ber.*, 1898, 31, 557—565. Compare this vol., i, 75 and 187). The action of substituted nitrosobenzenes on diazomethane has been studied in order to determine whether the nature and position of the substituting groups interfere with the formation of N-glyoxime ethers.

Glyoxime N-paratolylic ether is readily obtained when an ethereal solution of pure paranitrosotoluene is treated with an ethereal solution of diazomethane. *Glyoxime N-orthotolylic ether* crystallises in yellow needles or plates, melts at 188°, and when treated with alcoholic potash yields orthazoxytoluene melting at 59—60°. The authors have prepared a number of substituted hydroxylamines by reducing dilute alcoholic solutions of the nitro-compounds with zinc dust in the presence of ammonium chloride; the best yields (30—35 per cent.) are obtained when only about 5 grams are reduced at a time. On oxidation with chromic mixture, these compounds gave the corresponding nitroso-derivatives. 4-Nitrosometaxylylene, after distillation in steam, is obtained as a green oil which solidifies when cooled to 0°, and then melts at 47·5°. Glyoxime N-1 : 3 : 4-xylylic ether crystallises in yellow needles melting at 198°. 2-Hydroxylaminometaxylylene crystallises from light petroleum in colourless needles, melts at 98°, and on oxidation yields 2-nitrosometaxylylene melting at 144—145°. Hydroxylaminomesitylene melts at 105° when freshly crystallised, but at 95° when kept for 24 hours; Bamberger gives 116°. Nitrosomesitylene crystallises from dilute alcohol in rhombic plates melting at 129° (Bamberger gives 121·5—122·5°); when treated with diazomethane, it is reduced to hydroxylaminomesitylene, and yields no N-glyoxime ether.

1-Hydroxylamino-2 : 4 : 6-tribromobenzene crystallises in colourless needles, and melts and decomposes at 132°. Formaldehyde, glyoxal, or phenylhydrazine converts it into tribromaniline. When oxidised with chromic anhydride, it yields 1-nitroso-2 : 4 : 6-tribromobenzene melting at 120°, together with hexabromazoxybenzene and tribromobenzene. The nitroso-compound is sparingly soluble in most solvents, yields green solutions, and is not readily volatile with steam; it gives a red solution when boiled with alcoholic potash, and when treated with phenylhydrazine is reduced to tribromaniline. Glyoxime N-2 : 4 : 6-tribromophenylic ether, after being dissolved in boiling chloro-

form and precipitated with alcohol, forms pale yellow needles melting at 249.5° . It is much more stable than the simple ethers, and is not acted on when boiled with Fehling's solution or with sodium acetate and acetic anhydride. When warmed with alcohol and phenylhydrazine, it yields hydroxylaminotribromobenzene and glyoxal-*osazone*. *Hexabromazoxybenzene* is obtained when the mother liquor from nitrosotribromobenzene is allowed to remain for 2—3 days. After being dissolved in hot benzene and precipitated with alcohol, it forms glistening, reddish-yellow plates melting at 215° . When reduced with zinc dust and alcohol in the presence of ammonium chloride, it yields *hexabromhydrazobenzene*, which crystallises in colourless needles melting at 126 — 127° . It quickly turns red on exposure to the air, and is readily soluble in most solvents. When warmed with glacial acetic acid (8—10 parts) and finely divided potassium dichromate (1—1.5 parts) for 5—10 minutes on the water bath, it yields *hexabromazobenzene*, which crystallises in red needles melting at 213° .

2-Nitrosodimethyl-1:3:5-metaxyldine melts at 104° , and does not react with diazomethane. J. J. S.

Formation of Acetals from Diortho-substituted Aromatic Aldehydes. By EMIL FISCHER and GEORG GIEBE (*Ber.*, 1898, 31, 545—549).—The authors regard the formation of acetals from aldehydes as analogous to the etherification of acids by the aid of hydrogen chloride and an alcohol. They have, therefore, undertaken experiments in order to determine whether Meyer and Sudborough's generalisations can also be applied to the acetal formation of aromatic aldehydes. The method employed was that previously described (this vol., i, 167). It has been found that, not only orthonitrobenzaldehyde, but also 2:5-dichlorobenzaldehyde and 3:6-dichloro-2-nitrobenzaldehyde, when treated with a 1 per cent. solution of hydrogen chloride, yield the corresponding acetals more readily than benzaldehyde itself. 2:4:6-Tri-methylbenzaldehyde also yields an acetal, but not quite so readily as benzaldehyde. The amount of acetal formed was determined by separating the acetal from the unaltered aldehyde, by the aid of hydroxylamine.

2:5-Dichlorobenzodimethylacetal was obtained by dissolving 10 grams of the aldehyde in 40 grams of a 1 per cent. solution of hydrogen chloride in dry methylic alcohol, and allowing the mixture to remain for 22 hours at the ordinary temperature. It boils at 257 — 258° under a pressure of 750 mm., and when cooled to 0° solidifies, and then melts at 15° ; its sp. gr. = 1.274 at 18° . The yield was 83 per cent. of the theoretical.

3:6-Dichloro-2-nitrobenzodimethylacetal was prepared by dissolving 15 grams of the aldehyde in 75 grams of the warm methyl alcoholic hydrogen chloride solution, and allowing the mixture to remain for 24 hours at the ordinary temperature; the yield was 70 per cent. of the theoretical. It crystallises from light petroleum in needles, melts at 62 — 63° , and is readily soluble in alcohol or ether. The corresponding diethylacetal, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CH}(\text{OEt})_2$, was obtained in a similar manner, but as the aldehyde is only sparingly soluble in ethylic alcohol, a large excess of the latter must be taken (15 grams of alde-

hyde to 400 of alcohol); it crystallises from alcohol in colourless needles melting at 98—99°.

2:4:6-Trimethylbenzodimethylacetal boils at 242—243° (corr.) under 741 mm. pressure, and solidifies in a mixture of solid carbonic anhydride and ether. The yield was 32 per cent. of the theoretical. Under exactly the same conditions, benzaldehyde yields 53 per cent. of benzodimethylacetal boiling at 198—199° under a pressure of 762 mm. (compare Wicke, *Annalen*, 102, 363). When boiled with 20 times its weight of aqueous hydrochloric acid (2.5 per cent.), it is completely converted into the aldehyde. J. J. S.

2:5-Dichlorobenzaldehyde. By ROBERT GNEHM and RUDOLF SCHÜLE (*Annalen*, 1898, 299, 347—367. Compare Gnehm and Bänziger, *Abstr.*, 1896, i, 432).—2:5-Hexachlorohydrobenzamide, $(C_6H_3Cl_2 \cdot CH)_3N_2$, obtained by the action of alcoholic ammonia on dichlorobenzaldehyde, crystallises from hot acetone in long, silky needles; it melts at 167° (corr.), and is easily resolved into its components.

The α -naphthylamine compound of 2:5-dichlorobenzaldehyde is odourless, and melts at 111—112° (corr.); the β -naphthol compound, $C_6H_3Cl_2 \cdot CH(O \cdot C_{10}H_7)_2$, crystallises from glacial acetic acid in white prisms, and melts, evolving gas, at 205°.

Polymeric 2:5-dichlorothiobenzaldehyde is produced by the action of hydrogen sulphide on 2:5-dichlorobenzaldehyde; it is an amorphous powder, which dissolves readily in benzene, chloroform, and glacial acetic acid, and melts at 194—197°.

2:5-Dichloromandelonitrile, $C_6H_3Cl_2 \cdot CH(OH) \cdot CN$, is prepared from potassium cyanide and the sodium hydrogen sulphite compound of dichlorobenzaldehyde; it forms lustrous, white leaflets, and melts at 93°. It is very volatile in an atmosphere of steam.

2:5-Dichloromandelic acid, $C_6H_3Cl_2 \cdot CH(OH) \cdot COOH$, arises from the nitrile under the influence of concentrated hydrochloric acid at 130° in sealed tubes, alcoholic potash being without action on the substance; it crystallises from water in lustrous, white needles, and melts at 84° (corr.).

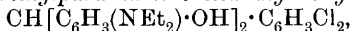
2:5-Dichlorodiparamidotriphenylmethane, $C_6H_3Cl_2 \cdot CH(C_6H_4 \cdot NH_2)_2$, obtained by heating dichlorobenzaldehyde with aniline and concentrated hydrochloric acid on the water bath, crystallises from petroleum, and melts at 107°. The hydrochloride crystallises in long needles, and the sulphate is sparingly soluble in water and alcohol. The diacetyl derivative crystallises from ethylic acetate in white needles, and melts at 212° (uncorr.).

2:5-Dichlorotriphenylmethane, $CHPh_2 \cdot C_6H_3Cl_2$, is produced by condensation of 2:5-dichlorobenzaldehyde with benzene; it crystallises from alcohol in long, well-formed prisms, and melts at 87° (corr.). 2:5-Dichlorophenylditolylmethane, $CH(C_6H_4Me)_2 \cdot C_6H_3Cl_2$, separates from alcohol in colourless crystals, and melts at 89° (corr.).

When a cooled solution of dichlorobenzaldehyde and phenol in glacial acetic acid is treated with concentrated sulphuric acid, the liquid becomes yellowish-red, and exhibits fluorescence; water precipitates a resin, which dissolves in soda, and is reprecipitated by carbonic anhy-

dride. Crystallisation from alcohol yields the substance in rosette-like aggregates, but it has not a constant melting point; it probably consists of the condensation product, $C_6H_3Cl_2 \cdot CH(C_6H_4 \cdot OH)_2$. Similar compounds are obtained from orthocresol and from resorcinol.

2 : 5-Dichlorotetraphenylparadiamidodihydroxytriphenylmethane,



is obtained by heating dichlorobenzaldehyde and diethylmetamidophenol with a solution of zinc chloride in glacial acetic acid during several hours at 130° ; it is an amorphous, reddish powder, and exhibits both basic and acidic properties. The *leuco*-compound is prepared by the action of concentrated sulphuric acid, which eliminates $1H_2O$; it is a blue, amorphous substance, and is readily oxidised in air.

2 : 5-Dichlororosaniline is produced when the *leuco*-compound is heated with concentrated sulphuric acid at 140 — 145° , then poured into water, and the filtered liquid boiled with ferric chloride. It separates from the aqueous solution in a gelatinous condition; the *nitrate* forms a bluish-red solution in water, exhibiting yellow fluorescence.

2 : 5-Dichlorobenzylidenic chloride, $C_6H_3Cl_2 \cdot CHCl_2$, prepared by slowly adding chlorosulphonic acid to a solution of dichlorobenzaldehyde in chloroform, crystallises from chloroform in cubes, and melts at 42° . Fuming sulphuric acid resolves it into dichlorobenzaldehyde and hydrogen chloride.

Although attempts to sulphonate tetramethyldiamido-2 : 5-dichlorotriphenylmethane were unsuccessful, treatment of the *leuco*-base with the monohydrate of sulphuric acid converts it into a mixture of mono-sulphonic and disulphonic acids; oxidation of this product with lead peroxide gives rise to an amorphous, greenish-blue colouring matter.

Benzaldehydeorthosulphonic acid, $SO_3H \cdot C_6H_4 \cdot COH$, is prepared according D.R.P. 88952 by heating orthochlorobenzaldehyde with sodium sulphite during 6 hours at 170 — 180° ; it is a thick syrup, which does not crystallise in the desiccator. The *sodium* salt crystallises from water in long, well-formed prisms; the *barium* salt crystallises in bundles of long prisms. The *phenylhydrazone* crystallises from water in long, slender needles melting at 174.5° (corr.); the *sodium* salt forms small, yellow needles. The *sodium* salt of the oxime crystallises in prisms containing $1H_2O$.

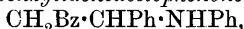
Benzaldehydeorthosulphonic acid combines with two molecular proportions of numerous amines, forming valuable colouring matters.

M. O. F.

Nitrogenous Derivatives of Benzylideneacetophenone. By JOSEF TAMBOR and F. WILDI (*Ber.*, 1898, 31, 349—354).—Benzylideneacetophenone readily forms additive compounds with ammonia and primary aromatic amines, but not with aromatic or mixed secondary bases. One molecule of the base reacts either with one or two molecules of benzylideneacetophenone.

Dibenzylideneacetophenonamine, $NH(CHPh \cdot CH_2Bz)_2$, crystallises in small needles melting and evolving gas at 163° , and yields an *acetyl*-derivative, which crystallises in white needles, and melts at 149° . Dibenzylideneacetophenonenitrotoluidine, prepared from nitrotoluidine [$Me : NR_2 : NO_2 = 1 : 2 : 5$], crystallises in sulphur yellow needles melt-

ing at 203° . The compound with orthonitraniline forms pale red needles melting at 243° , whilst that with metanitraniline melts and decomposes at $238-240^{\circ}$ and that derived from paranitraniline at $251-252^{\circ}$. *Dibenzylideneacetophenone- α -naphthylamine* crystallises in well-developed, greenish prisms melting at 180° . No compounds of 1 mol. of benzylideneacetophenone with 1 mol. of any of the foregoing amido-compounds could be obtained, whereas it readily unites with 1 mol. of aniline to form *benzylideneacetophenoneaniline*,



which crystallises in white needles melting at 175° . Similar behaviour is shown by paratoluidine, the compound with which forms silky needles melting at 172° , and by β -naphthylamine, which forms a compound melting at 200° . No other additive compounds could be obtained from the last three amido-compounds. A. H.

Etherification of Phenols and Benzenecarboxylic Acids. By HANS VON PECHMANN (*Ber.*, 1898, 31, 501-504).—When an ethereal or alcoholic solution of a benzenecarboxylic acid is poured into an ethereal solution of diazomethane, CH_2N_2 , nitrogen is evolved and the acid is completely converted into the methylic salt; this is the case even with mesitylcarboxylic, symmetrical tribromobenzoic, and mellitic acids (with symmetrical trinitrobenzoic acid, the nitro-groups are also attacked), all of which acids contain two substituting groups in the ortho-position relatively to the carboxyl group.

It is suggested that the reaction consists in a union of the diazomethane with the carboxyl group of the acid $\text{R}\cdot\text{COOH}$, to form a diazo-compound, $\text{R}\cdot\text{COO}\cdot\text{N}_2\cdot\text{CH}_3$, which then splits into $\text{R}\cdot\text{COOCH}_3 + \text{N}_2$, direct displacement of the H of the COOH group being thus effected. A similar direct replacement is effected in diortho-substituted acids when these yield metallic salts; from these salts, the ethereal salts can be prepared by treatment with alkyl iodides. Since the ethereal salts of such acids cannot be obtained by the action of alcohol and hydrochloric acid, it must be concluded that the formation of ethereal salts under such circumstances does not consist in a direct replacement, $\text{R}\cdot\text{COOH} + \text{EtOH} = \text{R}\cdot\text{COOEt} + \text{H}_2\text{O}$, but is preceded by the formation of an additive compound, $\text{R}\cdot\text{C}(\text{OH})_2\cdot\text{OEt}$ (Wegscheider, *Abstr.*, 1895, i, 499); it is easy to suppose that the formation of such a compound might be hindered by the presence of two groups in the ortho-position, although the direct displacement of the carboxylic hydrogen is not so hindered. C. F. B.

β -Isophenylacetic Acid. By EDUARD BUCHNER and FERDINAND LINGG (*Ber.*, 1898, 31, 402-403).—When ethylic ψ -phenylacetate, after fractionation under diminished pressure, is heated for 4 hours at 150° in tubes from which the air has been pumped out, and the product is distilled with steam, *ethylic β -isophenylacetate* passes over as an oil which boils at 115° under 15 mm. pressure. This yields anhydrous sodium β -isophenylacetate when it is hydrolysed with sodium ethoxide and a little water; the anhydrous *silver* salt was also prepared. By decomposing the sodium salt with cooled, dilute sulphuric acid, *β -isophenylacetic acid*, $\text{C}_8\text{H}_8\text{O}_2$, is obtained; this melts at $55-56^{\circ}$, is oxidised at once by permanganate in alkaline solution, and, on successive

treatment with phosphorus pentachloride and aqueous ammonia, yields an *amide* which melts at 98° (compare Abstr., 1897, i, 282).

C. F. B.

Calcium Mesitylenate, and the Author's Water of Crystallisation Theory. By THEODOR SALZER (*Ber.*, 1898, 31, 504—505).—Calcium mesitylenate is now found to crystallise with $5\text{H}_2\text{O}$ when it is precipitated at the ordinary temperature, and so is in accordance with Rule VI. of the author's theory (Abstr., 1895, 488).

A new rule, Rule VIII., is thus enunciated: "The normal calcium salts of all monobasic benzoic acid derivatives with substituting groups in the meta- or para-position, crystallise with at least $3\text{H}_2\text{O}$, whilst those of acids substituted in the ortho-position crystallise with only $2\text{H}_2\text{O}$." In analogy with this is the fact that the calcium salts of the substituted salts of the paraconic acids crystallise with $2\text{H}_2\text{O}$.

C. F. B.

Action of Ethylic Oxalate and Sodium Ethoxide on Substituted Nitrotoluenes. By ARNOLD REISSERT and JOH. SCHERK (*Ber.*, 1898, 31, 387—397. Compare Abstr., 1897, i, 417).—*Paranitrometatolylpyruvic acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{COOH}$ [$\text{Me} : \text{CH}_2 : \text{NO}_2 = 1 : 3 : 4$], is formed when a solution of 92 grams of sodium in 1840 grams of absolute alcohol is slowly added to a well-cooled mixture of 292 grams of ethylic oxalate and 302 grams of paranitrometaxylene and the mixture kept at about 40° for 3 days, the acid being best isolated in the manner previously described. The yield is only some 30 per cent. of the theoretical. It separates from glacial acetic acid in small crystals containing 1 molecule of acetic acid, which it loses at 100° , and then melts at 193° . It is sparingly soluble in water, somewhat more readily in benzene or chloroform, and dissolves with the greatest readiness in alcohol, ether, acetone, and acetic acid. The solutions of its alkali salts have a deep-red colour, its *barium* and *calcium* salts are reddish-yellow, its *lead* salt has a bright, orange-yellow colour. Its *phenylhydrazone* crystallises, on the addition of water to its alcoholic solution, in small, hard, yellow crystals melting and decomposing at 150° .

Paranitrometatoluenitrile is the product formed when hydrochloric acid (10 per cent.) is added to a boiling aqueous solution of the acid (1 mol.) and sodium nitrite (2 mols.); it begins to melt at 78° , but is not completely melted below 120° . It dissolves readily in alcohol, ether, acetic acid, or hot water, and, when shaken with concentrated sulphuric acid and benzene containing thiophen, gives a deep-blue solution. When an alkaline solution of orthonitrometatolylpyruvic acid is oxidised with hydrogen peroxide, *paranitrometatolylacetic acid* is formed; this melts at 149° , and is readily soluble in alcohol, ether, acetone, and chloroform. When chromic acid mixture is used as the oxidising agent, *paranitrometatolualdehyde* is formed; this can be purified by distillation with steam, when it crystallises in thin, glistening needles melting at 61° . The yield is very poor. Its *phenylhydrazone* melts at 150° . When paranitrometatolylacetic acid (10 grams) is suspended in water (200 grams) and reduced with 100 grams of hydrochloric acid (10 per cent.) and the requisite quantity of granulated tin, *paramethyl-*

oxindole, $C_6H_3Me\begin{smallmatrix} <CH_2 \\ NH \end{smallmatrix}>CO$ [Me:NH=1:4], is the chief product; the mixture is heated for an hour in a reflux apparatus, filtered, the filtrate rendered alkaline and extracted with ether; the residue from the ethereal extract is recrystallised from hot water, and the methyl-oxindole is obtained in the form of needles melting at 168° , its *acetyl* derivative, $C_{11}H_{11}NO_2$, crystallises from water in yellowish needles, and melts at 161° .

Orthonitrometatolylic methylic ether crystallises from light petroleum in glistening needles, melts at 55° , and is readily soluble in the usual organic solvents. Its condensation with ethylic oxalate is best accomplished by the following process. Ethylic oxalate (7.3 grams) is gradually added to a mixture of sodium ethoxide (3.4 grams) which is quite free from alcohol, with dry ether (34 grams), a solution of the methylic ether (8.4 grams) in dry ether is then added, and the whole allowed to remain for 2 days; the mass is extracted with water, and, on acidifying, the aqueous extract, *orthonitrometamethoxyphenylpyruvic acid*, is precipitated; a further quantity may be obtained by extracting the acidified solution with ether. It crystallises from acetic acid in small, yellowish crystals melting at 128° , is sparingly soluble in water, but dissolves readily in ether, alcohol, acetone, or acetic acid.

Ethylic orthonitrophenylacetate, obtained by etherifying the acid formed on oxidising orthonitrophenylpyruvic acid with hydrogen peroxide (Abstr., 1897, i, 417), crystallises from alcohol in long needles melting at 69° .

When ethylic oxalate (29.2 grams) is mixed with a cold solution of sodium (9.2 grams) in absolute alcohol (180 grams), and orthonitrotoluidine (15.3 grams) is added to the mixture, a considerable quantity of *sodium orthonitroparatolyloxamate*,

$NO_2 \cdot C_6H_3Me \cdot NH \cdot CO \cdot COOH$ [Me:NO₂:NH=1:2:4], crystallises out at the end of 24 hours. The *free acid* melts at 179° , and is fairly easily soluble in hot water. Its ethylic salt is obtained when ethylic oxalate is boiled with orthonitrotoluidine.

If, in the above condensation, the substances are used in the proportion of 1 mol. of orthotoluidine, 2 of sodium ethoxide, and 1 of ethylic oxalate, a certain amount of *diorthonitrodiparatolyloxamide* is formed, together with the oxamic acid. It crystallises from acetic acid in small needles, and is very sparingly soluble in the usual solvents.

J. J. S.

Action of Ethylic Oxalate and Sodium Ethoxide on Nitrotolylic Methylic Ether. By ARNOLD REISSERT (*Ber.*, 1898, 31, 397—398. Compare preceding abstract). — Paranitrometatolylic methylic ether, $NO_2 \cdot C_6H_3Me \cdot OMe$ [OMe:Me:NO₂=3:1:4], crystallises from alcohol or light petroleum in yellow needles melting at 51 — 52° . When this ether (16 grams), in absolute alcoholic solution, is treated with ethylic oxalate (29.2 grams) and a solution of sodium (9.2 grams) in absolute alcohol (184 grams), and the mixture is kept for 3 days in a closed flask at 35 — 40° , *paranitrometamethoxyphenylpyruvic acid*, $NO_2 \cdot C_6H_3(OMe) \cdot CH_2 \cdot CO \cdot COOH$, is formed and can be isolated

in the usual manner. It separates from glacial acetic acid in pale yellow crystals containing a molecule of acetic acid and melting at 161° . Its *ethylic* salt melts at 142° , and its *phenylhydrazone* crystallises in yellow needles melting at 107 — 108° . J. J. S.

α -Acetylcoumarin. By E. RAP (*Gazzetta*, 1897, 27, ii, 498—502).—On heating a mixture of salicylaldehyde and ethylic acetoacetate with acetic anhydride for 8 hours on the water bath, pouring the product into water, and adding sodium carbonate, *α -acetylcoumarin*, $\text{CH}:\text{CH}\cdot\text{C}(\text{CH}_3):\text{CH}:\text{CAc}$, is obtained; it crystallises in long, white needles melting at 123 — 124° , and yields iodoform when treated with iodine and potash. The *phenylhydrazone*, $\text{C}_{11}\text{H}_8\text{O}_2\cdot\text{N}_2\text{HPh}$, which is readily prepared, crystallises in yellow needles melting at 181 — 182° .

On treating *α -acetylcoumarin* with bromine dissolved in carbon bisulphide, addition occurs, followed by evolution of hydrogen bromide and separation of *β -bromo- α -acetylcoumarin*, $\text{C}_6\text{H}_4\text{C}(\text{CHBr})\text{CH}(\text{COAc})$, which probably results from the decomposition of an intermediate additive product of the constitution $\text{C}_6\text{H}_4\text{C}(\text{CHBr})\text{CH}(\text{COBr})$; it crystallises in long needles which melt at 161 — 162° , decomposes at 166° , and yields salicylic acid on fusion with potash.

On distilling the commercial salicylaldehyde employed, a considerable fraction was obtained at 100 — 194° ; and this, when treated as above with ethylic acetoacetate, yields a substance which crystallises in large prisms melting at 103 — 104° , apparently identical with the additive compound, $\text{C}_7\text{H}_6\text{O}_2\cdot\text{C}_4\text{H}_6\text{O}_3$, of salicylaldehyde with acetic anhydride obtained by Perkin. It gives a compound with phenylhydrazine melting at the same temperature as the hydrazone of salicylaldehyde.

W. J. P.

Action of Aniline on Dihydroxytartaric Acid. By ARNOLD REISSERT (*Ber.*, 1898, 31, 382—387).—Blank's anilidomalonic acid, $\text{NHPh}\cdot\text{CH}(\text{COOH})_2$ (D.R.P. 95268), is obtained by the action of aniline on dihydroxytartaric acid. Fifty c.c. of hydrochloric acid (25 per cent.) are carefully added to a mixture of 20 grams of sodium dihydroxytartrate and 1 litre of water, so that no evolution of carbonic anhydride ensues. Aniline (22.5 grams) is added, the mixture left overnight and then extracted 8—10 times with ether. The residue from the ethereal extractions is dissolved in a small quantity of warm alcohol and aniline; on cooling, the *aniline* salt crystallises in the form of small needles melting at 127° ; a considerable amount, however, remains in solution and may be precipitated by the addition of light petroleum. The free acid is obtained by dissolving the aniline salt, in the cold, in the least possible quantity of hydrochloric acid (25 per cent.), and then adding an equal volume of water; it is best purified by dissolving it in alcohol and precipitating with light petroleum. When its aqueous solution is boiled for some time, it is decomposed into carbonic anhydride and *anilidoacetic acid* melting

at 125°. The *ammonium* salt is one of the most characteristic salts of anilidomalonic acid.

Anilidomalonanilic acid, $\text{NHPh}\cdot\text{CH}(\text{COOH})\cdot\text{CO}\cdot\text{NHPh}$, is obtained in a somewhat similar manner when a larger quantity, namely, 42 grams, of aniline, is used; at the end of about 2 hours the precipitate is removed, dissolved in very dilute sodium hydroxide solution, and reprecipitated with hydrochloric acid; a further amount may be obtained from the mother liquors. It crystallises in minute needles, melts and decomposes at 157°, is sparingly soluble in the usual organic solvents, and insoluble in water. The reactions of solutions of the ammonium salt with various metallic salts are given. Anilidoacetanilide is obtained when the previous compound is added to 10 times its weight of water, then poured into an equal volume of concentrated sulphuric acid, and the mixture heated in a boiling water bath, when anilidoacetanilide sulphate separates. J. J. S.

Phthalonic Acid. By CARL GRAEBE and F. TRÜMPY (*Ber.*, 1898, 31, 369—375).—Phthalonic acid (orthocarboxyphenylglyoxylic acid), $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COOH}$, is best obtained by Tcherniac's method (compare this vol., i, 263, and also 201). Naphthalene (100 grams), potassium permanganate (625 grams), and water (6.25 litres) are boiled for 3—4 hours in a large, leaden reflux apparatus. When colourless, the solution is cooled, the excess of naphthalene removed, and the clear solution, after acidifying with sulphuric acid (222—240 grams H_2SO_4), is evaporated to dryness and then extracted with ether. The ethereal residue consists of phthalic and phthalonic acids, which are easily separated by treatment with a small quantity of water in which phthalonic acid is readily soluble. 80—95 grams of dry phthalonic acid and 8—10 grams of phthalic acid may thus be obtained.

Phthalonic acid crystallises with $2\text{H}_2\text{O}$, which it loses when heated at 80—100°, more rapidly at 110—120°; in the hydrated form, it begins to melt at 50°, but when anhydrous melts at 144.5° (corr.). It forms syrupy supersaturated solutions with the greatest readiness; a solution saturated at 15° contains 115 parts of the anhydrous acid to 100 parts of water. It is readily soluble in alcohol or ether and sparingly in chloroform. When the acid is heated, the chief products are phthalaldehydic acid and its anhydride, together with phthalic anhydride and diphtalyl, $\text{CO}\langle\text{O}\rangle\text{C}_6\text{H}_4\text{C}:\text{C}\langle\text{O}\rangle\text{C}_6\text{H}_4\text{CO}$. On the addition of benzene containing thiophen in solution and of concentrated sulphuric acid to phthalonic acid, an intense red coloration is developed; on adding water, however, the benzene layer becomes colourless. When the acid is evaporated to dryness on the water-bath with an excess of ammonia, a yellow residue is obtained; this dissolves in water, and on the addition of hydrochloric acid, an excess of which is to be avoided, a white precipitate of an *acid*, $\text{C}_9\text{H}_7\text{NO}_4$, is thrown down. This melts and decomposes at 90—100°, is sparingly soluble in water but dissolves in alcohol, yielding an intense yellow solution which becomes deeper in colour on the addition of alkali. Its *calcium* and *silver* salts indicate that it is a dibasic acid, probably having the constitution $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NH})\cdot\text{COOH}$.

When an aqueous solution of phthalonic acid is treated with an excess of hydroxylamine hydrochloride (2 mols.) and the requisite quantity of sodium carbonate, and is acidified at the end of two days, crystals of phthalimide are thrown down.

Phthalonic acid oxime, $\begin{array}{c} \text{O} \\ | \\ \text{CO} \cdot \text{C}_6\text{H}_4 \end{array} \text{---N} \gg \text{C} \cdot \text{COOH}$, may be obtained by extracting the aqueous solution with ether; it melts at 167—168°, and dissolves in alkalis and alkali carbonates, yielding deep red solutions, which readily decompose on warming, yielding phthalimide and phthalamic acid.

Phthalidecarboxylic acid is formed when phthalonic acid is reduced in alkaline, neutral or acid solution; it is most readily prepared by the aid of zinc and hydrochloric acid. When heated at 200°, it is completely converted into phthalide and carbonic anhydride.

Phthalaldehydic acid is readily obtained by the action of sodium hydrogen sulphite on phthalonic acid. Ten grams of the dry acid, 55 c.c. of a 10 per cent. sodium carbonate solution, and 30 c.c. of a concentrated solution of sodium hydrogen sulphite are warmed together on the water bath, then evaporated to dryness, acidified, and the aldehydic acid extracted with ether. The yield is 55—60 per cent.

J. J. S.

Homophthalic Acid. By CARL GRAEBE and F. TRÜMPY (*Ber.*, 1898, 31, 375—377).—Phthalonic acid (10 grams), red phosphorus (2 grams), hydriodic acid of sp. gr. = 1.67 (12 c.c.), and water (3 c.c.) are heated for 3—4 hours in a reflux apparatus; a further quantity of water (15—18 c.c.) is then added to the hot mixture, which is boiled until all the precipitated acid has dissolved. The solution is filtered hot, and, on cooling, the greater part of the homophthalic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{COOH}$, crystallises in a pure state. When heated to about 190°, the acid is converted into its anhydride, and this, when heated at 210—230°, is converted into hydrodiphthalolactonic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CO}$.

Gabriel's deoxybenzoin- β -carboxylic acid is readily obtained by the action of benzene and aluminium chloride on homophthalic anhydride; 10 grams of the anhydride, 100 of benzene, and 12 of aluminium chloride, are heated for 3 hours in a reflux apparatus, water and hydrochloric acid are added, and the excess of benzene removed by distillation with steam.

J. J. S.

Action of Ethylic Oxalate on Paramidophenol and its Ethers. By ARNALDO PIUTTI and R. PICCOLI (*Ber.*, 1898, 31, 330—336).—According to Castellaneta (*Abstr.*, 1896, 1, 367), oxalic acid and its ethereal salts react with paramidophenols to form a substituted diamide and monamide, but no imide, whereas Wirths (*Abstr.*, 1897, i, 145) states that he obtained a substituted diamide and an imide. The authors have therefore again investigated the action of diethylic oxalate on paramidophenol and its derivatives, and have in no case obtained a derivative of oximide.

Ethylic oxalate and paramidophenol react at 160° to form dipara-

hydroxyphenyloxamide, which has been described by Castellaneta under this name, and by Wirths as oxalylparamidophenol, together with *ethylic parahydroxyphenyloxamate*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{COOEt}$, melting at $184-185^\circ$. The latter crystallises in long, vitreous, monosymmetric prisms [$a : b : c = 0.81902 : 1 : 0.65750$; $\beta = 84^\circ 23'$]. When heated with hydrochloric acid at 100° , it yields oxalic acid, paramidophenol, and ethylic chloride, whilst concentrated ammonia converts it into *parahydroxyphenyloxamide*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$, which crystallises in slender, colourless needles, and sublimes and partly decomposes at about 266° . With ethylic oxalate, paranisidine yields *ethylic paramethoxyphenyloxamate*, which melts at $108-109^\circ$, and crystallises in lustrous, colourless, asymmetric prisms [$a : b : c = 1.61646 : 1 : 1.19475$; $\alpha = 95^\circ 44' 54''$; $\beta = 86^\circ 8' 15''$; $\gamma = 96^\circ 18' 43''$]. This compound was described by Wirths as oxalylparanisidine; concentrated ammonia converts it into *paramethoxyphenyloxamide*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$, which separates from alcohol in white flakes melting at 241° . Paraphenetidine reacts with ethylic oxalate to form *ethylic parethoxyphenyloxamate* (the oxalylparaphenetidine of Wirths), which melts at $108-110^\circ$, and crystallises in large, six-sided, monosymmetric lamellæ [$a : b : c = 1.32727 : 1 : 0.95580$]. Alcoholic ammonia converts it into *parethoxyphenyloxamide*, which melts at 241.5° , whilst it is decomposed in the normal manner by hydrochloric acid.

A. H.

Action of Acetic Anhydride on the Anilides of Dibasic Acids. By HANS VON PECHMANN and WILHELM SCHMITZ (*Ber.*, 1898, 31, 336—337. Compare this vol., i, 135).—Acetic anhydride in presence of sodium acetate converts oxanilide into vinylideneoxanilide, as already described, but does not act in a similar manner with the anilides of other dibasic acids. Thus carbanilide and malonanilide yield acetanilide, whereas succinanilide is converted into succinanil.

A. H.

Synthesis of Diphenylhydantoin. By W. HENTSCHEL (*Ber.*, 1898, 31, 508—510. Compare Bischoff and Hausdörfer, *Abstr.*, 1892, 1334).—When carbonylic chloride is passed into a 30 per cent. solution of ethylic phenylamidoacetate in benzene, the carbaminic chloride, $\text{COOEt} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{COCl}$, is formed; it separates from a mixture of petroleum and alcohol in large prismatic crystals, and melts at 60° . The compound is converted into ethylic carbanilphenylamidoacetate by heating with aniline on the water bath, and when this salt is repeatedly crystallised from alcohol, it yields diphenylhydantoin.

M. O. F.

Aromatic Sulphonamides. By FRANZ A. H. SCHREINEMAKERS (*Rec. Trav. Chim.*, 1897, 16, 411—424).—In the preparation of mesitylenesulphonic chloride, the author has always obtained a quantity of a colourless substance insoluble in ether but soluble in chloroform, ethylic acetate, or acetone; this he regards as the sulphonic anhydride. To prepare the amide, a weighed quantity of concentrated ammonia of known strength is placed in a flask and covered with a layer of ether, a portion of the required quantity of the sulphonic chloride is added; after shaking and allowing to remain for some time until the odour

of ammonia has disappeared, a strong solution of the requisite quantity of potassium hydroxide is added to decompose the ammonium chloride; a further quantity of the sulphonic chloride is then added, and the processes repeated until nearly all the ammonia has been converted into the amide. The methylamide and ethylamide may be obtained in a similar manner.

Mesitylenesulphonmethylamide crystallises from dilute alcohol in long needles melting at $89-90^{\circ}$; the yield is some 85 per cent. of the theoretical. *Mesitylenesulphondimethylamide* also crystallises in colourless needles and melts at 45° . *Mesitylenesulphonethylamide* melts at 75° . None of these amides are decomposed by aqueous potash. When heated with water, they all have the property of forming liquids not miscible with water; the temperature of transition for the methylamide is $76-77^{\circ}$, for the dimethylamide, $40-41^{\circ}$, and for the ethylamide, $64-65^{\circ}$; the presence of other substances raises or lowers these transition temperatures.

Pseudocumenesulphonmethylamide is less readily soluble in ether and alcohol than the corresponding mesitylene derivative. It melts at $90-91^{\circ}$, and its transition temperature in water is $79-80^{\circ}$. The *dimethylamide* is even less soluble in ether, and it melts at $115-116^{\circ}$. The *ethylamide* melts at 98° , its transition temperature being 88° . Both monomethyl and monethyl derivatives dissolve in alkalis, but are reprecipitated on the addition of hydrochloric acid.

Metaxylenesulphonic chloride melts at 32° (Jacobsen, *Ber.*, 1877, 10, 1015, gives 34°), the amide at 137° , and the methylamide at 43° ; the latter is readily soluble in alcohol or ether, its transition temperature is $32-33^{\circ}$. The *dimethylamide*, prepared in the usual manner, remains liquid for several weeks, but when placed in a freezing mixture it slowly solidifies, and then melts at 35° .

Parabenzoyloxybenzenesulphonic chloride, obtained by warming Engelhardt and Latschinow's sodium parabenzoyloxybenzenesulphonate (*Zeit. Chem.*, 1868, 76) with phosphorus pentachloride, and recrystallising from ether, melts at $115-116^{\circ}$. The corresponding *amide* is sparingly soluble in ether, alcohol, or water, and melts at $234-236^{\circ}$. If, in the preparation of the amide, an excess of ammonia is employed and the mixture is warmed, benzamide is produced. When the amide is hydrolysed with barium hydroxide solution, *parahydroxybenzenesulphonamide* is formed, and, after recrystallisation from alcohol or water, melts at $176-177^{\circ}$.
J. J. S.

Unsaturated Hydrocarbons. By REINHOLD WALTHER (*J. pr. chem.*, 1898, [ii], 57, 111-112).—On heating benzylic cyanide with benzaldehyde at 200° , the elements of water are given off, and, at a slightly higher temperature, the cyanogen group is hydrolysed and carbonic anhydride eliminated. By a similar reaction, stilbene has been obtained from benzaldehyde and phenylacetic acid, and the author proposes to prepare a number of hydrocarbons and acids by this method.
A. W. C.

Paradinitrodibenzylidisulphonic Acid. By CHRISTOPH RIS and CARL SIMON (*Ber.*, 1898, 31, 354-355. Compare this vol., i, 143).—Sodium dinitrodibenzylidisulphonate is converted by hot concentrated

hydrochloric acid into the hydrogen sodium salt, and not into the free acid, and it appears that it was this salt which was described by Green and Wahl as the free acid (this vol., i, 200); the latter, which can readily be prepared by the action of sulphuric acid on the barium salt, forms a readily soluble, leafy, crystalline mass, which does not deliquesce. The substance described by Green and Wahl as dinitrostilbenedisulphonic acid is also a hydrogen sodium salt, and appears to have the composition $C_{14}H_9N_2O_9S_2Na$, its constitution having not yet been ascertained. The authors claim priority for their work.

A. H.

Fluorescent Substances. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, 31, 310—311).—The compound, $C_{26}H_{18}O_4$, is obtained by heating resorcinol with benzylic chloride on the water bath, and extracting the product repeatedly with water, alcohol, methylic alcohol, and a mixture of alcohol and glacial acetic acid; it is a red, amorphous powder which does not melt below 320° . The alcoholic solution exhibits a beautiful, green fluorescence, and the red solution in alkalis also develops green fluorescence on dilution; it dissolves in warm, concentrated sulphuric acid, forming a yellow solution which exhibits green fluorescence on dilution. The *tetracetyl* derivative is a yellow, amorphous substance which melts at 90 — 100° .

M. O. F.

Paratoluoylorthobenzoic Acid. By HEINRICH LIMPRICHT (*Annalen*, 1898, 299, 300—315. Compare Abstr., 1895, i, 422).—The barium salt of paratoluoylorthobenzoic acid crystallises from water in aggregates of flattened prisms containing $4H_2O$, the crystals becoming opaque in the desiccator without losing water. The *methylic* salt crystallises in rectangular plates and melts at 66° .

Paratoluoylorthobenzoic acetic anhydride, $C_6H_4Me \cdot CO \cdot C_6H_4 \cdot COOAc$, obtained by heating dehydrated toluoylbenzoic acid with acetic anhydride on the water bath, forms colourless crystals, and melts at 102° . When heated at 200° , it yields acetic and phthalic anhydrides.

Phenyltolylphthalide, $\begin{matrix} C_6H_4 \\ CO \cdot O \end{matrix} > CPh \cdot C_6H_4Me$, is produced on warming a solution of toluoylbenzoic acetic anhydride in benzene with aluminium chloride; it separates from ether in transparent crystals and melts at 106° .

Nitroparatoluoylorthobenzoic acid, $NO_2 \cdot C_6H_3Me \cdot CO \cdot C_6H_4 \cdot COOH$, separates from dilute alcohol in colourless crystals containing $1H_2O$; it melts at 205° , and crystallises from glacial acetic acid in colourless prisms. The barium salt contains $1H_2O$, and the *ethylic* salt crystallises from alcohol in prisms and melts at 122° . The *chloride* crystallises in aggregates of colourless needles and melts at 142° ; the *amide* decomposes at 200° , and the *anhydride* melts at 203° .

Nitrotoluoylbenzoic acetic anhydride, $NO_2 \cdot C_6H_3Me \cdot CO \cdot C_6H_4 \cdot COOAc$, separates from alcohol in colourless, prismatic crystals and melts at 145 — 146° .

Trinitroparatoluoylorthobenzoic acid is obtained by nitrating toluoylbenzoic acid with a mixture of sulphuric and nitric acids.

Amidoparatoluoylorthobenzoic acid, $NH_2 \cdot C_6H_3Me \cdot CO \cdot C_6H_4 \cdot COO H$

forms colourless crystals and melts at 163° ; the *hydrochloride* and *silver* derivative are crystalline. M. O. F.

Ditolyolphthalide. By HEINRICH LIMPRICHT (*Annalen*, 1898, 299, 286—299).—Ditolyolphthalide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{O} \end{smallmatrix} \text{C}(\text{C}_6\text{H}_4\text{Me})_2$, is obtained in almost theoretical amount by treating equal parts of toluene and phthalic chloride in carbon bisulphide with aluminium chloride; it separates from alcohol in colourless, transparent crystals and melts at 116.5° .

Phenylditolylmethanecarboxylic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\text{Me})_2$, prepared from ditolyolphthalide by the action of alcoholic potash and zinc dust, crystallises from dilute alcohol in slender needles, and melts at 168° . The *ethylic* salt softens at 183° and melts at 197 — 198° .

Tolymethylantranol, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4\text{Me}) \\ \text{C}(\text{OH}) \end{smallmatrix} \text{C}_6\text{H}_3\text{Me}$, is produced by the action of concentrated sulphuric acid on phenylditolylmethanecarboxylic acid; it crystallises from alcohol and melts at 117° .

Tolymethyloxanthranol, $\text{C}_6\text{H}_4\text{Me}\cdot\text{C} \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \\ \text{O} \end{smallmatrix} \text{C}\cdot\text{OH}$, obtained by oxidising tolylmethylantranol with chromic acid in glacial acetic acid solution, forms yellowish, microscopic needles, and melts at 207° . The *acetyl* derivative softens at 50° and melts at 87° .

Tolymethylantracene, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4\text{Me}) \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_3\text{Me}$, is formed on heating tolylmethyloxanthranol with zinc dust in an atmosphere of hydrogen; it sublimes in large, transparent, lustrous leaflets, and melts at 191° .

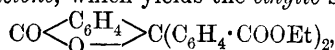
Dinitroditolyolphthalide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{O} \end{smallmatrix} \text{C}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_2$, prepared by adding ditolyolphthalide to cold fuming nitric acid, crystallises from a mixture of alcohol and ether in lustrous, monoclinic prisms and melts at 132° ; the *octonitroditolyolphthalide*, which is formed when nitration is effected with a mixture of sulphuric and nitric acids, crystallises in microscopic needles, and melts at 289° .

Diamidoditolyolphthalide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{O} \end{smallmatrix} \text{C}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2)_2$, obtained by reducing the dinitro-derivative with stannous chloride in alcoholic hydrochloric acid, crystallises from alcohol in small, lustrous prisms, and melts at 192° . The *hydrochloride* melts at 280° , and the *sulphate* forms white crystals.

Dihydroxyditolyolphthalide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{O} \end{smallmatrix} \text{C}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OH})_2$, is formed from the diamido-derivative on treating its acid solution with sodium nitrite and warming the liquid with copper powder; it separates from alcohol as a brown, crystalline powder, and decomposes when heated.

Triphenylcarbinoltricarboxylic acid, $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{COOH})_3$, is prepared by oxidising ditolyolphthalide with chromic and acetic acids, removing

the portion of the product which does not dissolve in alkali, and completing the oxidation of the soluble substances with potassium permanganate; it begins to melt, and decomposes, at 165°, becoming solid at 180°, and finally melting at 304°. This decomposition involves the formation of the *lactone*, which yields the *ethylic* salt,



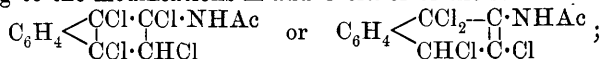
melting at 138—139°. The *amide* of the tricarboxylic acid crystallises in long prisms and melts at 309°. M. O. F.

Chloro- and Bromo-derivatives of β -Naphthylamine. By ADOLPH CLAUS and OSKAR JÄCK (*J. pr. Chem.*, 1898, [ii], 57, 1—18).—On passing chlorine into a well-cooled solution of β -acetonnaphthalide in chloroform or acetic acid, Claus and Philipson (*Abstr.*, 1891, 461) obtained 1-chloro-2-acetonnaphthalide, which was converted by an excess of chlorine into its tetrachloride without forming a dichloroacetonnaphthalide. When, however, chlorine (2 mols.) was passed into β -naphthylamine dissolved in 80 per cent. sulphuric acid, 1':4':2-dichloramidonaphthalene was obtained. The authors have confirmed the constitution of this compound by converting it, by means of the diazo-reaction, into the 1':4':2-trichloronaphthalene of Armstrong and Wynne (*Proc.*, 1890, 16).

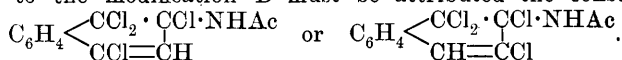
When dry air, saturated with bromine, is passed into a solution of β -naphthylamine in 80 per cent. sulphuric acid, the 1':3':2-dibromonaphthylamine, obtained by Claus and Philipson (*loc. cit.*) by the action of bromine on an acetic acid solution of β -naphthylamine, is formed; in the latter case, however, 1:2-bromonaphthylamine was first produced, whereas in the former no trace of a monobromo-derivative can be detected. The authors find also that when 1:2-bromamidonaphthalene is dissolved in sulphuric acid, it is not acted on by either chlorine or bromine, and that 1:2-chloronaphthylamine is, under the same conditions, also unaffected by chlorine. They hence conclude that, in presence of sulphuric acid, 2 mols. of chlorine or of bromine act simultaneously on β -naphthylamine.

When 1:2-chloroacetonnaphthalide tetrachloride is heated with alcoholic potash or soda, resinous products only are formed; when, however, aqueous sodium hydroxide (1 mol.) is employed, hydrogen chloride is separated, and three isomeric *dichloro-2-acetonnaphthalide dichlorides*, $\text{C}_{12}\text{H}_9\text{Cl}_4\text{NO}$, are obtained. The first of these (A) melts at 99—100°, and is easily soluble in ether; it is almost the sole product when the temperature of the reaction is not allowed to rise above 65°. At 80°, the second modification (B) predominates; this is insoluble in ether, but crystallises from alcohol in monoclinic pyramids, and melts at 145°. Together with B is formed the third modification (C), which crystallises from alcohol in prisms and melts at 163°. The modification (A) decomposes rapidly in the air with the loss of HCl, forming 1:3:4-trichloro-2-acetonnaphthalide, which crystallises from alcohol in colourless, lustrous needles and melts at 220°. The same substance is obtained when the third modification (C) is heated above 100°. The second modification (B) is only decomposed when heated above its melting point, a resinous product being obtained. These facts can be explained

by giving to the modifications A and C either of the formulæ



whilst to the modification B must be attributed the constitution



When 1-chloro-2-acetonaphthalide tetrachloride is heated with an excess of aqueous soda, a *compound*, $\text{C}_9\text{H}_5\text{ClO}_2$, is formed, which appears to be an indene derivative; it sublimes in beautiful, yellow needles, which darken when heated to 120° , and possess no definite melting point. This substance yields a *sodium* salt which crystallises from water in blood-red needles, and a *barium* salt which forms copper-coloured needles. Its investigation is being continued.

1:3:4-*Trichloro-2-naphthylamine*, obtained by heating the alcoholic solution of its acetyl compound with hydrochloric acid, crystallises in slender, white needles, and melts at 175° .

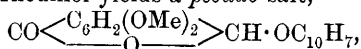
1-Bromo-2-acetonaphthalide tetrachloride, prepared by passing chlorine (2 mols.) into 1-bromo-2-acetonaphthalide dissolved in chloroform, melts and decomposes at 115° .

A *dibromo-β-naphthaquinone* is formed when 1:3':4-tribromo-2-naphthylamine is diazotised in hydrochloric acid and the product boiled with water; it crystallises from light petroleum in orange-yellow needles or plates, and on being heated darkens at 120 — 130° and melts and decomposes at 200° . From the fact that it is not acted on by alkalis or ammonia, whereas 3-bromo-β-naphthaquinone is converted by these reagents into derivatives of α-naphthaquinone (Zincke, Abstr., 1887, 53), its constitution seems to be that of a 4:3'-*dibromo-1:2-naphthaquinone*. This view supports that taken by Claus and Philipson (*loc. cit.*) of the constitution of the tribromonaphthylamine from which it was prepared. 4:3'-*Dibromo-1:2-dihydroxynaphthalene*, formed when the quinone is heated with aqueous sulphurous acid in a sealed tube at 120 — 130° , crystallises from water in needles, and when heated, decomposes without melting.

1:4:3'-*Tribromonaphthalene*, prepared by heating dry 1:4:3'-tribromo-2-diazonaphthalene sulphate with absolute alcohol, crystallises from hot water in iridescent plates, melts at 98° , and sublimes in the form of slender, white needles.

W. A. D.

Some Ethereal Salts and a Crystalline Pseudo-salt of Rhodinol. By ERNST ERDMANN (*Ber.*, 1898, 31, 356—360). The ethereal salts of rhodinol are best prepared by the action of the acid chloride on the alcohol in presence of pyridine. The *butyrate* boils at 142 — 143° under a pressure of 13 mm., the *isobutyrate* at 135 — 137° under the same pressure, the *isovalerate* at 135 — 138° at 7 mm., and the *palmitate* at about 260° , under a pressure of 12 mm. When heated with opianic acid, rhodinol yields a *pseudo-salt*,



which crystallises from alcohol in slender needles melting at 48.5° , and is slowly hydrolysed by boiling water.

A. H.

Composition of the Ethereal Oil of *Monarda Fistulosa* L. By EDWARD KREMERS (*Chem. Centr.*, 1897, ii, 41).—From the red to brownish oil, of sp. gr. = 0.941 at 20°, obtained by distilling *Monarda fistulosa*, the author isolated carvacrol and a red, crystalline substance which melted at 219–223°, and with alkalis behaved like alizarin. Cymene was also detected. E. W. W.

Composition of the Oil of *Monarda Fistulosa* L. By E. J. MELZNER and EDWARD KREMERS (*Chem. Centr.*, 1897, ii, 41; from *Pharm. Review*, 1896. Compare preceding abstract).—A table showing the physical properties and content of phenols (carvacrol), of samples of oil prepared at different seasons is given. After the phenols had been removed, the oil, which contains no ethereal salts, was fractionated, and the physical properties of the various fractions are also shown in a table. E. W. W.

Composition of the Oil of *Monarda Punctata* L. By W. R. SCHUMANN and EDWARD KREMERS (*Chem. Centr.*, 1897, ii, 42; from *Pharm. Review*, 1896).—By distilling *Monarda punctata* L. with steam, the author has obtained a pale yellow oil which has an odour of mint, sp. gr. = 0.9307 at 20° and specific rotatory power $[\alpha]_D = +0.0588^\circ$. The oil yielded 56 per cent. of thymol when shaken with sodium hydroxide solution and the remaining oil had a sp. gr. = 0.887 at 20° and specific rotatory power $[\alpha]_D = +1.716^\circ$; cymene was detected in the first fractions of this oil, and linalool or a similar compound in the higher fractions. E. W. W.

Composition of the Oils obtained from *Sassafras* Bark and from *Sassafras* Leaves. By FREDERICK B. POWER and CLEMENS KLEBER (*Chem. Centr.*, 1897, ii, 42; from *Pharm. Review*, 1896).—By distilling the air-dried *sassafras* bark, 7.4 per cent. of a yellow to a reddish-yellow oil of sp. gr. = 1.075 at 15° and rotatory power $[\alpha]_D = +3^\circ 16'$ (100 mm. tube) was obtained, whilst the roots, freed from bark, yielded only 0.9 per cent. of oil. About 78 per cent. of safrole was obtained from the oil by freezing. By shaking the residual oil with sodium hydroxide solution, 0.5 per cent. of eugenol was isolated, and, finally, 10 per cent. of pinene and phellandrene together was found in the lower fractions, but neither dipentene nor cineol could be detected. The so-called safrene is apparently a mixture of pinene with a little phellandrene. The higher fractions of the oil obtained from the root contain dextrorotatory camphor, and the last fractions give a violet coloration with sulphuric acid and glacial acetic acid, but as the sesquiterpene contained in the oil from the bark does not yield a solid hydrochloride, the presence of cadinene is doubtful. The content of camphor (6.8 per cent.) was estimated by reducing to borneol, converting into the ethoxy-derivative and saponifying.

Only 0.028 per cent. of a pale yellow oil was obtained from the leaves; it had the odour of lemons, a sp. gr. = 0.872 at 15° and rotatory power $[\alpha]_D = +6^\circ 25'$. When the oil was shaken with sodium hydrogen sulphite, a crystalline substance was formed which yielded citral on being decomposed. By heating the residual oil with alcoholic

potassium hydroxide solution and distilling in steam, a paraffin melting at 58° remained behind, and in the alkaline solution acetic and isovaleric acids were detected. The lower fractions of the oil contain, besides pinene and phellandrene, the aliphatic terpene myrcene (compare *Pharm. Rund.*, March, 1895); the higher fractions of the saponified oil contain linalool and geraniol, and the last distillates a sesquiterpene which does not yield a solid hydrochloride. E. W. W.

Guaiacum Resin. I. By JOSEF HERZIG and F. SCHIFF (*Monatsh.*, 1897, 18, 714—721).—The results summarised in a previous paper (Abstr., 1897, i, 254) are dealt with at length.

The acid of guaiacum resin (guaiaretic acid) is best prepared by extracting the resin (1 kilogram) successively with sodium hydrogen carbonate (500 grams), water, and ether, then dissolving it in benzene (1 kilogram), and adding light petroleum (5 litres); a resinous mass is precipitated, which is filtered off and the solution evaporated, the residue being dissolved in alcohol and alcoholic potash added; after 24 hours, 60 grams of potassium guaiarate has separated, more (16 grams) of this being obtained from the mother liquor, and (50 grams) from the precipitate formed as above on the addition of petroleum to the benzene solution. A much cleaner product is obtained by this method than by that of Hlasiwetz (compare Doebner and Lückér, Abstr., 1897, i, 65).

The authors show that the benzoyl derivative described as a monobenzoate by Doebner and Lückér (*loc. cit.*) is really a *dibenzoate*, $C_{20}H_{24}O_4Bz_2$, analogous to the diacetate described in the previous paper; it melts at 132 — 135° , not at 131° . They are unable to confirm the statement that guaial (tiglic aldehyde) is formed on distilling guaiaretic acid, guaiacol and pyroguaiacin alone being obtained. Methylic chloride and catechol are formed when guaiaretic acid is heated with hydrochloric acid and acetic acid at 140° ; a small quantity of *norguaiaretic acid*, $C_{18}H_{22}O_4$, was also formed. The latter is best prepared by heating guaiaretic acid with concentrated hydriodic acid (b. p. = 127°), and separates from dilute alcohol in white needles, melts at 185° , and yields a *tetracetate*, $C_{18}H_{18}(OAc)_4$, which crystallises from alcohol in white needles and melts at 100 — 102° .

Analyses of the compounds described point to the formula $C_{20}H_{26}O_4$ for guaiaretic acid, rather than $C_{20}H_{24}O_4$, as given by Doebner.

W. A. D.

Morin, and the Constitution of Flavone Derivatives. By JOSEF HERZIG (*Monatsh.*, 1897, 18, 700—713).—Since morin differs from quercetin and other flavonol derivatives in colour, and in its behaviour with bromine in acetic acid or alcoholic solution, and with acetic anhydride, the author considers that it cannot have the formula $\begin{array}{c} \text{CH(OH)} \cdot \text{CH} \cdot \text{C} - \text{O} \cdot \text{C} \cdot \text{C}_6\text{H}_3(\text{OH})_2 \\ \text{CH} \cdot \text{CH(OH)} \cdot \text{C} \cdot \text{CO} \cdot \text{C(OH)} \end{array}$ [$\text{C}:\text{OH}:\text{OH} = 1:2:4$], at-

tributed to it by Perkin (*Trans.*, 1896, 792). He also discusses the influence of the hydroxyl groups in determining the properties of flavonol derivatives, and considers that, amongst this class of compounds, should be included, at present, only substances which closely resemble chrysin and fisetin in physical as well as chemical properties.

It is pointed out that Perkin (*loc. cit.*), in his determination of the

methoxyl groups in tetrabromomorin ethylic ether, omitted to allow for the 2 mols. of water which the ether retains after being dried either in a vacuum or at 100°. That this water is retained by the crystals only, and not chemically as a hydrate, is shown by an analysis of the *tetracetyl* derivative of the ether, $C_{15}H_5Br_4O_2(OAc)_4 \cdot OEt$, which is anhydrous, and melts at 116—120°.

Tetrabromomorin, prepared by the action of bromine on morin in acetic acid solution, melts at 258°, and is identical with the product obtained by Benedikt and Hazura (Abstr., 1885, 533) by the hydrolysis of its ether. Tetrabromomorin ethylic ether, on digestion with hydriodic acid, is reduced to morin, which melts at 285°; under similar conditions, dibromoquercetin tetraethylic ether and dibromorcinol diethylic ether are converted into quercetin and orcinol respectively.

The author points out that, although tetrabromomorin is rapidly converted into its monethylic ether when bromine is added to its alcoholic solution, no such change takes place on heating it with alcohol and hydrochloric or hydrobromic acid, morin, under the same conditions, being also unaffected. The formation of tetrabromomorin monethylic ether by the action of bromine on morin dissolved in alcohol is therefore due to a specific action of bromine.

W. A. D.

Occurrence of Choline and Trigonelline in *Strophanthus* Seeds. Preparation of Strophanthin. By HERMANN THOMS (*Ber.*, 1898, 31, 271—277).—The seeds of *Strophanthus hispidus* (which are used in West Africa for preparing arrow-poison) were powdered in a mortar, freed from fat and oil, of which they contain 25 per cent., by pressing and washing with light petroleum, and extracted with cold 70 per cent. alcohol in a percolator. The alcohol was distilled off, the residue extracted with water, and lead acetate added to the aqueous extract so long as a precipitate was produced. To the filtered solution, pure ammonium sulphate was added cautiously, in order to precipitate the excess of lead, and then a large excess of powdered ammonium sulphate; the strophanthin separates in flakes, which collect on the walls as a pasty mass; it is purified by repeated solution in alcohol and precipitation with ether. So prepared, it is amorphous, free from nitrogen, and neutral in reaction; it is very poisonous.

The filtrate from the strophanthin was acidified strongly with sulphuric acid, mixed with potassium bismuthiodide solution, and the precipitate, after being washed with dilute sulphuric acid, was decomposed with silver carbonate and water, and the filtered solution mixed with hydrochloric acid, again filtered, and evaporated to crystallisation. In this way, the hydrochlorides of the two bases were obtained; one of them, which is soluble in absolute alcohol, is choline hydrochloride; the other, of which 4.2 grams were obtained from 3 kilos. of seeds, is insoluble in alcohol, and was found to be identical with the hydrochloride of trigonelline (Jahns, Abstr., 1888, 166), the methylbetaine of nicotinic acid.

C. F. B.

Choline and Trigonelline in the Seeds of *Strophanthus* Kombé. By HERMANN THOMS (*Ber.*, 1898, 31, 404).—The presence of these bases has been shown in the same manner as in the case of *S. hispidus* (preceding abstract).

C. F. B.

Strophanthin. By LEOPOLD KOHN and VICTOR KULISCH (*Ber.*, 1898, 31, 514—516).—The authors ascribe to strophanthin the empirical formula $C_{31}H_{48}O_{12}$. Hydrolysis with mineral acids resolves it into strophanthidin, along with a product which reduces Fehling's solution, but gives none of the characteristic reactions of dextrose.

M. O. F.

Strophanthin and Strophanthidin. By FRANZ FEIST (*Ber.*, 1898, 31, 534—541. Compare preceding abstracts).—Strophanthin from kombé seeds has the properties previously described by Fraser (*Abstr.*, 1887, 1115; 1888, 606; 1890, 262). It is free from nitrogen, does not reduce Fehling's solution, is optically inactive, readily absorbs moisture, and is capable of forming several hydrates. It loses part of this water when placed over sulphuric acid or when gently warmed, but the last portions of water are difficult to remove. After drying over sulphuric acid, it melts and decomposes at 170° ; the author suggests the formula $C_{32}H_{48}O_{16}$. When hydrolysed, strophanthin yields strophanthidin which is insoluble in water, and a compound, $C_{13}H_{24}O_{10}$, which is readily soluble in water, besides a sugar or mixture of sugars; it has been proved that only minute quantities of glucose exist in the hydrolysed solution. The compound, $C_{13}H_{24}O_{10}$, melts at 207° , dissolves with the greatest readiness in water, is also soluble in hot ethylic alcohol or acetone, very sparingly in methylic alcohol, and practically insoluble in ether or light petroleum; it reduces Fehling's solution only after prolonged boiling, does not react with phenylhydrazine, is not directly fermented by yeast, and is slightly dextrorotatory $[\alpha]_D = +8^{\circ} 24'$ (in 5.76 per cent. solution). On oxidation, it yields oxalic acid, but neither saccharic nor mucic acid, and when boiled with hydrochloric or with sulphuric acid at 120° , it gives a product which reduces Fehling's solution. When benzoylated by the Schotten-Baumann method, it yields a *dibenzoyl* derivative melting at 136° , and a compound, $C_{20}H_{22}O_8$, melting at 68° .

A solid sugar melting at 95° was also isolated from the aqueous solution; it was separated from the compound, $C_{13}H_{24}O_{10}$, by its solubility in methylic alcohol. It reduces Fehling's solution, but does not yield a sparingly soluble osazone.

Strophanthidin melts at 169 — 170° , decomposes at 176° , and on again cooling melts at 232° . It has the composition $C_{26}H_{33}O_7 + 1\frac{1}{2}H_2O$, and on drying readily loses $1H_2O$. It dissolves in concentrated sulphuric acid, yielding a brick-red solution, does not reduce Fehling's solution, and decolorises bromine but slowly. When oxidised with chromic anhydride, it yields benzoic acid, but on oxidation with alkaline permanganate the chief products are oxalic and acetic acids. When hydrolysed by boiling with alkali solution and then acidified, a mixture of two compounds is obtained. The chief product ($C_{24}H_{30}O_5 + 1\frac{1}{2}H_2O$) is a yellow, crystalline substance melting and decomposing at 294° ; in the anhydrous form, it decomposes at 350 — 360° without melting. When freshly prepared, it is readily soluble in sodium carbonate, but after some time it can only be dissolved by warming with alkali; it is readily soluble in alcohol and acetone, more sparingly in methylic alcohol, and is insoluble in light

petroleum or ether. When heated with a 3 per cent. solution of hydrogen chloride in alcohol, it yields a white, amorphous substance with a high melting point.

A second compound, $(C_7H_{10}O_2)_x$, obtained on hydrolysis, is much more readily soluble in methylic alcohol; it crystallises in needles, melts at 198.5° , and is insoluble in sodium carbonate, but dissolves in sodium hydroxide solution. It dissolves in concentrated sulphuric acid, yielding a brick-red solution, and on the addition of water a blue, flocculent precipitate is obtained. It is also soluble in concentrated nitric acid, and the addition of water to this solution causes no precipitate (difference from strophanthidin).

Bromine reacts with an ethereal solution of strophanthidin, yielding two bromo-compounds, one, $C_{39}H_{51}Br_5O_{10}$, colourless and melting at 126° , the other, $C_{39}H_{33}Br_{11}O_4$, yellow, and melting at 160° . Both are readily soluble in chloroform, acetone, alcohol, or ether, but insoluble in water or light petroleum. When oxidised with bromine and sodium hydroxide, strophanthidin yields a *dibasic acid*, $C_{39}H_{54}Br_2O_{10}$, melting at 163° .

Alkaline permanganate converts strophanthidin into an amorphous substance, soluble in alkali, alcohol, and chloroform, but insoluble in water, ether, light petroleum, or cold acetone. Its melting point is above 300° .

J. J. S.

Gambierfluorescein and Gambier-catechu-red. By KARL DIETERICH (*Chem. Centr.*, 1897, ii, 50—51; from *Ber. Pharm. Ges.*, 7, 153—161).—*Gambierfluorescein* is prepared by moistening 5 grams of gambier-catechu with water, decomposing with 20 per cent. sodium hydroxide solution, and shaking with benzene or ether; the latter dissolves, not only the fluorescein, but also two other substances, the one of an oily and the other of a waxy nature. Gambierfluorescein is purified by treating with sulphuric acid, decomposing with sodium hydroxide, and extracting with ether. Its solution becomes red in contact with the air, and, on evaporation, yields a red tar similar to a phlobaphen; this the author names gambier-catechu-red. The fresh alcoholic solution of gambierfluorescein is green by reflected and yellow by transmitted light. Gambierfluorescein, which contains no nitrogen, is insoluble in water and alkalis, but dissolves in acids; the solutions are not fluorescent. When a solution of it, in light petroleum, is cooled, white needles separate, but on drying they turn red and partly lose their crystalline structure. It is contained in the catechu either in the form of a catechin or of a catechutannic acid compound, or in both forms, the compound, which must be analogous in composition to a salt, becoming saponified in the process of extraction. Pegu-catechu does not contain this substance, and the main difference between these catechus is that, whilst gambier-catechu-red is not contained as such in gambier catechu, pegu-catechu-red is actually contained in pegu-catechu.

Gambier-catechu-red is a reddish-brown, resinous powder, which floats on water, becomes electrified by friction, melts at 130 — 131° , is insoluble in ether, forms a blood-red solution in sulphuric acid, but neither yields fluorescent solutions nor possesses the basic character of

gambierfluorescein. If a faintly acid solution in alcohol be neutralised with alcoholic potassium hydroxide, an intensely dark blue, fluorescent solution is produced, similar to that of tincture of turmeric, but the colour disappears on adding more alkali or on warming. Gambiercatechu-red does not give a precipitate with tannic acid. The acetyl number shows that it still contains hydroxyl groups. The fatty oil obtained from the catechu by means of benzene has an acid number = 14.89, ether number = 43.33, and a saponification number = 58.22; the iodine number is very low. E. W. W.

Colouring Matter of the Red Grape. By LIVIO SOSTEGNI (*Gazzetta*, 1897, 27, ii, 475—485).—The author has extracted a red colouring matter from a red Italian wine, and also from the cœnocyanin of commerce. The colouring matter is precipitated from the cœnocyanin by hydrochloric acid and purified by repeatedly precipitating it from alcoholic solution by ether; it is ultimately obtained in amorphous, transparent, red granules, and is readily oxidised by atmospheric oxygen. When dried in a vacuum over sulphuric acid, it has the composition $C_{19}H_{16}O_{10}$, corresponding with Gautier's ampelochroic acid (*Abstr.*, 1892, 1242), but on drying at 150° , it seems to be converted into an *anhydride* of the composition $C_{38}H_{30}O_{19}$. On boiling the substance, $C_{19}H_{16}O_{10}$, in dilute sulphuric acid solution, it is converted into the anhydride, but no pure product could be isolated with more concentrated acid. The colouring matter forms salts with copper, silver, and potassium, but their composition could not be definitely determined; it yields phloroglucinol on heating with aqueous potash, and also combines with bromine. W. J. P.

β -Naphthoquinoline. By ADOLPH CLAUS and HEINRICH BESSELER (*J. pr. chem.*, 1898, [ii], 57, 49—67).— β -Naphthoquinoline, $\begin{array}{c} \text{CH} \text{---} \text{C} \text{---} \text{N} \text{:CH} \\ || \quad | \\ \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} \text{:CH} \end{array}$, prepared by Skraup's method (*Monatsh.*, 1883, 4, 437), crystallises from light petroleum in almost colourless, nacreous leaflets melting at 94° and boiling at 340° . The *methiodide* forms yellow, glistening needles melting and decomposing at 186° ; the *methochloride* crystallises from water in colourless needles melting at 138 — 140° , but if previously dried at 120° does not melt until 236° ; the *methodichromate* forms small, yellow needles melting and decomposing at 232° , and the *methosulphate*, prepared by the action of silver sulphate on the methiodide, is exceedingly soluble in water, and could not be obtained crystalline.

β -Naphthoquinoline *ethobromide*, produced when the free base is heated with ethylic bromide in sealed tubes for 3—4 hours at 95° , crystallises from methylic or ethylic alcohol in regular octahedra containing alcohol of crystallisation. From amylic alcohol, it crystallises in colourless needles melting at 238° . The *ethiodide* forms yellow needles melting and decomposing at 206° , and the *ethodichromate* yellow, microscopic needles melting and decomposing at 212° .

β -Naphthoquinoline *benzylchloride* forms amber-coloured prisms or plates melting at 196° , and the *benzylodichromate* melts at 200° .

All these salts contain water of crystallisation when crystallised from water.

When treated with alkalis in aqueous solution, the alkylated β -naphthoquinolines yield, as do the simple quinolines, quaternary alkylidenequinolinium bases, none of which have been, so far, prepared in a pure condition, but it is hoped that this end may be obtained by repeating the experiments with larger quantities of material.

By the oxidation of the alkylidene bases of β -naphthoquinoline with potassium ferricyanide or mercuric oxide, alkylquinolones are produced. *Methyl- β -naphthoquinolone* separates from alcohol in small, glistening, greenish-yellow crystals melting and decomposing at 183° .

β -Naphthoquinoline methiodide, on treatment with moist silver oxide, gives a strongly basic solution not containing anything soluble in ether and free from iodine, showing that no alkylidene base is formed. This is a striking difference from the simple quinoline derivatives, which, on treatment with moist silver oxide, give the corresponding methylenequinolinium base, readily soluble in ether.

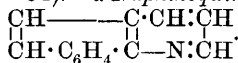
2"-Bromo- β -naphthoquinoline, prepared by the Claus-Collischonn method, is readily soluble in alcohol, ether, and chloroform, crystallises in long, silken needles, melts at 117 – 118° , and sublimes unchanged. On oxidation with chromic acid, it yields β -bromonicotinic acid, thus proving the 2-position of the bromine atom in the pyridine ring. The *methiodide* forms small, yellow needles melting at 225° . Towards alkalis and silver oxide, it behaves like the naphthoquinoline derivatives already mentioned. The *methochloride* melts at 237° .

Nitro- β -naphthoquinoline, obtained as the sole product of nitration of the free base, crystallises from alcohol in yellowish, silky needles melting at 165° . On oxidation with chromic acid, nicotinic acid is produced, showing nitration to have taken place in the naphthalene ring. The *methiodide* forms beautiful, glistening needles, becoming brown on heating to 150° , and melting and decomposing at 210° . The *methochloride* crystallises from alcohol in transparent, glistening plates or prisms melting at 218° .

Amido- β -naphthoquinoline, prepared by the reduction of the above nitro-compound, forms long, yellow crystals melting at 158° , and decomposing on exposure to light. It can be easily diazotised, and on boiling the diazo-sulphate with dilute sulphuric acid, the corresponding *oxy*-compound melting at 208 – 211° is obtained. The *methiodide* forms garnet-red, glistening plates or prisms melting at 237° , and the *methochloride* small, red crystals melting at 256° . The alkylated nitro- and amido- β -naphthoquinolines show the same behaviour towards alkalis and silver oxide as the alkylated naphthoquinolines. This will be dealt with more fully later.

A. W. C.

α -Naphthoquinoline. By ADOLPH CLAUS and PAUL IMHOFF (*J. pr. chem.*, 1898, [ii], 57, 68–84).— *α -Naphthoquinoline*,



The preparation of this substance by Skraup's method presents especial difficulties. It is a pleasant smelling base readily soluble in the ordinary organic solvents, crystallises from alcohol in colourless leaflets melting at 51° and boiling at 338° (uncorr.), and decomposes much more readily than β -naphthoquinoline. The *hydrochloride* forms

small, colourless needles melting at 213° ; the *disulphate* crystallises from alcohol in glistening plates or prisms melting at 213° ; the *nitrate* forms beautiful, silky needles melting at $135\text{--}137^{\circ}$; the *dichromate* yellow, glistening plates decomposing at 130° ; and the *platinochloride* small, yellow needles melting and decomposing at 224° .

α -Naphthoquinoline methiodide, obtained by heating the components for 5 hours at 115° in sealed tubes, crystallises from water or alcohol in beautiful, golden-yellow, glistening plates or needles melting at 179° ; the *methochloride* forms colourless, prismatic needles melting at 133° ; the *methodichromate* crystallises from water in orange-red, glistening needles decomposing at 190° , and the *methosulphate* in small, white needles melting at 162° .

On hydrolysis with alkalis, the alkylated α -naphthoquinolines are quantitatively converted into the methylene- α -naphthoquinolinium, but with moist silver oxide a substance is produced readily soluble in ether, thus showing a marked difference from the similar α -naphthoquinoline derivatives, probably due to a difference in constitution. The reaction is, however, very complicated, and before a satisfactory explanation is forthcoming, it must be much more fully studied.

Methyl- α -naphthoquinolone prepared by the oxidation of α -naphthoquinoline methiodide with mercuric oxide or potassium ferrocyanide in alkaline solution, crystallises from alcohol in glistening needles possessing a peculiar green colour and melting at 175° . It is not acted on by hot or cold dilute hydrochloric acid, but is dissolved by the concentrated acid, and yields a *platinochloride* which melts and decomposes at 262° .

α -Naphthoquinoline-3'-sulphonic acid, $\begin{array}{c} \text{C}(\text{SO}_3\text{H}) \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} - \text{N} \cdot \text{CH} \end{array}$, obtained

by the action of fuming sulphuric acid on the free base, forms beautiful, white crystals. Neither the acid nor its *potassium, sodium, barium*, or *silver* salt melts below 300° . The *methylic* salt separates from alcohol in small, colourless needles melting at 127° .

α -Naphthoquinoline-3'-sulphonic chloride forms yellow crystals melting at 116° . This substance which the authors propose to further investigate, was converted in the ordinary way into the *sulphonamide*, which forms small, glistening, colourless prisms melting at 225° .

3'-Hydroxy- α -naphthoquinoline, obtained by fusing the sulphonic acid with potash, crystallises from alcohol in glistening needles showing no sharp melting point; it blackens when heated to 240° , and melts and decomposes about 270° . The *hydrochloride* forms glistening, orange-yellow needles.

On nitration, α -naphthoquinoline yields two isomeric *mononitro*-derivatives in which the nitro-groups are in positions 3' and 4' respectively. The one crystallises in colourless needles melting at 151° , the other in yellow needles melting at 138° . Both yield nitrates melting respectively at 178° and 173° .

A. W. C.

Structural Relationships of the Two Naphthoquinolines. By ADOLPH CLAUS (*J. pr. chem.*, 1898, [ii], 57, 85—94).—In discussing at some length the probable constitution of the isomeric naphthoquinolines, the author points out that whereas Kekulé's benzene configura-

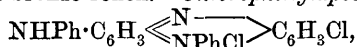
tion shows only one possible difference, namely, that the nitrogen atom of the pyridine ring is combined with different carbon atoms of the naphthalene ring, the "central" benzene formula allows a second and more substantial difference depending on the distribution of the central bonds. That some such important difference does exist seems probable from the varied behaviour of the naphthoquinolines on oxidation with chromic acid, and of their alkylated derivatives on treatment with alkalis or silver oxide.

The further study of this problem affords an opportunity for testing the efficacy of the central formula, of which the author proposes to take advantage.

A. W. C.

Relationship of Safranines, Isorosindulines, and Rosindulines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1898, 31, 299—308. Compare *Abstr.*, 1897, i, 636).—The authors have shown (*loc. cit.*) that rosindone and aposafranine are converted by phosphorus pentachloride into chloronaphthophenazonium chloride and chlorophenylphenazonium chloride respectively. The change is now found to be a general one for the indones of this series.

Dichlorophenylphenazonium chloride, $C_6H_3Cl \llcorner \begin{smallmatrix} N \\ \text{NPhCl} \end{smallmatrix} \gg C_6H_3Cl$, [N : N : Cl : Cl = 1 : 2 : 4 : 4], is obtained by dissolving safranol in five times its weight of phosphorus oxychloride, and treating it with phosphorus pentachloride (2 mols.); it crystallises from alcohol in reddish-yellow needles which exhibit a bluish reflex. The *nitrate* crystallises in steel-blue leaflets, and the *aurochloride* forms golden leaflets. When the aqueous solution is boiled with sodium acetate, *chloraposafranone*, $O \llcorner \begin{smallmatrix} C_6H_3 : N \\ \text{NPh} \end{smallmatrix} \gg C_6H_3Cl$, is produced; it crystallises from alcohol in brown prisms with bronze reflex. *Chlorophenylaposafranine*,



obtained by treating an alcoholic solution of dichlorophenylphenazonium chloride with aniline, crystallises from water in highly lustrous, yellow needles, and forms a green solution in concentrated sulphuric acid. The *platinochloride* is almost black, and has a metallic lustre.

Chlorophenylnaphthophenazonium chloride, $C_6H_3Cl \llcorner \begin{smallmatrix} N \\ \text{NPhCl} \end{smallmatrix} \gg C_{10}H_6$, is obtained from isorosindone, phosphorus oxychloride, and phosphorus pentachloride; it crystallises from a mixture of alcohol and ether in long, brownish-yellow needles, and separates from water with $1H_2O$. The *bromide* forms brownish-red, lustrous plates, and the *iodide* is dark-green; the *nitrate* crystallises in brown plates, the *platinochloride* separates from hot water in slender, brick-red needles, and the *aurochloride* is also red. Aniline converts the alcoholic solution of the chloride into phenylisosinduline hydrochloride.

Methylic bromide converts phenylrosinduline at 100° into a methobromide which is resolved by alcoholic potash into rosindone and methylaniline. Phenylisosinduline, on the other hand, yields a

methobromide, which is converted first into an unstable hydrate; the latter then undergoes oxidation into methylanilidorosindone.

Isorosindone *methiodide* crystallises from alcohol in lustrous needles, and loses methyl iodide at 170—180°. The *platinochloride* crystallises in reddish-brown needles, and the *aurochloride* forms red needles; the nitrate crystallises in leaflets having a green lustre, and becomes red when powdered. Alcoholic potash regenerates isorosindone from the methiodide, and also gives rise to *methoxyrosindone*,

$$\text{O} \left\langle \begin{array}{c} \text{C}_{10}\text{H}_5\text{N} \\ | \\ \text{NPh} \end{array} \right\rangle \text{C}_6\text{H}_5\cdot\text{OMe}$$
, which crystallises from a mixture of benzene and alcohol in reddish-brown leaflets containing benzene, and melts at 264—265°; the *methiodide* separates from alcohol in brown crystals having a green reflex. Concentrated sulphuric acid at 170° converts methoxyrosindone into hydroxyrosindone. M. O. F.

3-Hydroxy-1:2:4-triazole and Acetylsemicarbazides. By OSKAR WIDMAN and ASTRID CLEVE (*Ber.*, 1898, 31, 378—381).—*Diformylsemicarbazide*, $\text{N}(\text{CHO})_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is obtained when acetonesemicarbazone is boiled for some 4 hours with a large excess of the strongest formic acid (sp. gr. = 1.23). After the excess of formic acid has been distilled off, the product is crystallised from alcohol, when it forms colourless prisms melting at 158°, readily soluble in alcohol or water, but insoluble in ether. It gives a bluish-green precipitate with Fehling's solution but does not reduce it.

3-Hydroxy-1:2:4-triazole, $\begin{array}{c} \text{CH:N} \\ | \\ \text{NH:N} \end{array} \gg \text{C}\cdot\text{OH}$, is formed when acetonesemicarbazone is boiled for about 8 hours with a smaller quantity of concentrated formic acid; the residue, after the greater part of the formic acid has been distilled off, is cooled and rubbed with a small quantity of alcohol, when it yields crystals of the triazole; this melts at 234°, is readily soluble in alcohol or water, but insoluble in ether, and has acid but not basic properties. Its *silver* salt, $\text{C}_2\text{HN}_3\text{OAg}_2$, *basic copper* salt, $\text{O}(\text{Cu}\cdot\text{O}\cdot\text{C}_2\text{H}_2\text{N}_3)_2 + \text{H}_2\text{O}$, and *diacetyl* derivative crystallising in needles and melting at 137° are described.

Acetylsemicarbazide, $\text{NHAc}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is obtained when finely powdered, free semicarbazide is warmed on the water bath with acetic anhydride until all has dissolved. On the addition of alcohol, the acetyl derivative crystallises in small, hard, nodular masses; it melts at 165°, and is soluble in ether. *Isobutyrylsemicarbazide* melts at 163° and *benzoylsemicarbazide* crystallises in rhombic plates melting at 225°. These compounds cannot be converted into triazoles on account of the ease with which they are hydrolysed. The acetyl compound is hydrolysed by boiling with water, and the others when boiled with acids or alkalis. J. J. S.

Methyldioxytriazine. By ADRIANO OSTROGOVICH (*Gazzetta*, 1897, 27, ii, 416—429).—The author has previously shown (*Abstr.*, 1896, i, 261, 393) that methyldioxytriazine is formed on heating acetylurethane with carbamide. It is now shown that acetylcarbamide, acetylbiuret, and cyanuric acid are formed at the same time; on heating acetylcarb-

amide with urethane at 180—185°, methyldioxytriazine, acetylbiuret, and cyanuric acid are also obtained.

Acetylbiuret, on treatment with potash in alcoholic solution, yields a *potassium* derivative, $\text{NHAc}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, KOH, which crystallises in colourless needles; it is soluble in boiling alcohol but partially hydrolyses, giving potassium acetate and biuret; the corresponding *sodium* compound was prepared. By the action of sodium ethoxide on an alcoholic solution of acetylbiuret, a *substance* of the composition $\text{NHAc}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, EtONa, is obtained as a white, crystalline powder.

Methylic methyldioxytriazine, $\text{NH}\begin{smallmatrix} \text{CMe}=\text{N} \\ \text{CO}\cdot\text{NMe} \end{smallmatrix}\text{CO}$, obtained by heating the silver derivative of methyldioxytriazine with methylic iodide and methylic alcohol in a closed tube at 100°, crystallises with $1\text{H}_2\text{O}$ in minute, white crystals and is hydrolysed by potash with formation of methylamine. It was not obtained by heating acetylurethane with methylcarbamide at 140—145°, but methylacetylcarbamide was formed.

Ethylic methyldioxytriazine, $\text{C}_6\text{H}_9\text{N}_3\text{O}_2$, is obtained by the action of ethylic iodide on methyldioxytriazine at ordinary temperatures; it forms minute, white crystals, and yields ethylamine on hydrolysis with potash.

On treating acetylbiuret with acetic chloride, reaction occurs in accordance with the equation $\text{C}_2\text{H}_4\text{AcN}_3\text{O}_2 + 2\text{AcCl} = \text{HCl} + \text{CO}_2 + \text{AcOH} + \text{C}_3\text{HMe}_2\text{N}_3\text{O}$, HCl, *dimethyloxytriazine hydrochloride* being produced; this crystallises in needles, is very soluble in water, and forms a *platinochloride* which crystallises in large, yellow prisms. The free *base*, $\text{C}_5\text{H}_7\text{N}_3\text{O} + \text{H}_2\text{O}$, is obtained in large prisms and the *sulphate* crystallises either anhydrous or with $1\text{H}_2\text{O}$. The *sodium* salt $\text{C}_5\text{H}_6\text{N}_3\text{ONa} + 2\text{H}_2\text{O}$, and the *barium* salt, $(\text{C}_5\text{H}_6\text{N}_3\text{O})_2\text{Ba} + 7\text{H}_2\text{O}$, crystallise in colourless needles. On treating a solution of the base or one of its compounds with bromine, a *compound*, $\text{C}_5\text{H}_4\text{Br}_3\text{N}_3\text{O} + \text{H}_2\text{O}$, crystallising in white scales, is obtained.

W. J. P.

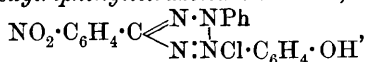
Methods of Formation of Paranitrodiphenyltetrazole. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 473—479. Compare Abstr., 1896, i, 630).—Paranitrodiphenyltetrazole, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{NPh} \\ \text{N}\cdot\text{N} \end{smallmatrix}$, can be

prepared by the following methods.

I.—When alcoholic solutions of nitrobenzylidenehydrazone and diazoparanisidine chloride are mixed, *paranitroparamethoxyformazylbenzene*, $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is produced in lustrous, brown needles which melt at 199° and form a deep green solution in sulphuric acid. When this compound is treated in chloroform solution with alcoholic hydrogen chloride and nitrous acid, it forms a *chloride* which does not crystallise, but yields, with potassium iodide, a yellow precipitate of *paranitroparamethoxytriphenyltetrazolium iodide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{NPh} \\ \text{N}\cdot\text{N}\cdot\text{NI}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \end{smallmatrix}$, which softens at 139—140°,

melts at 166—168°, and is sparingly soluble in most solvents. The impure chloride is converted by fuming nitric acid at 140—150°, into

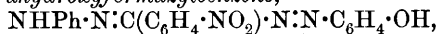
paranitroparahydroxytriphenyltetrazolium chloride,



which crystallises in pale yellow needles, melts at 208—209°, and decomposes at 233°. When this compound is converted into the *nitrate*, by precipitation with silver nitrate, and then oxidised by potassium permanganate in acid solution, it yields *paranitrodiphenyltetrazole* as a white, crystalline powder melting at 199—200°.

II.—The same nitrotetrazole can be obtained more readily by treating paranitroguanazylbenzene with concentrated nitric acid at 30—40°.

Paranitroparahydroxyformazylbenzene,



obtained when the nitrohydroxytriphenyltetrazolium chloride described above is reduced by ammonium sulphide, forms slender, brownish-red, matted needles melting at 194°.

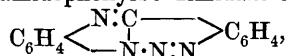
When paranitrobenzylideneamidoguanidine is treated with nitric acid in a similar manner to paranitroguanazylbenzene, it yields a substance which is probably a *dinitrobenzylideneamidoguanidine*, $\text{C}_8\text{N}_6\text{H}_8\text{O}_4$; this crystallises in yellow needles melting at 248—249°.

A. H.

New Method of Preparing Tetrazine Derivatives. By ALFRED JUNGAHN (*Ber.*, 1898, 31, 312—313. Compare Pinner, this vol., i, 94).—Tetrazine derivatives are formed by the action of hydrazine on thiamides. The amide is dissolved in alcohol and heated with aqueous hydrazine in a reflux apparatus during 1 hour.

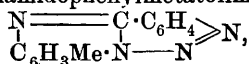
M. O. F.

Azimido-derivatives of Benzimidazoles. By STEFAN VON NIEMENTOWSKI (*Ber.*, 1898, 31, 314—323. Compare this vol., i, 210).—The *azimide* of β -orthamidophenylbenzimidazole,



is obtained in quantitative yield on adding alkali nitrite to an alcoholic solution of orthamidobenzimidazole acidified with hydrochloric acid, or by warming a neutral, alcoholic solution of the imidazole with amylic nitrite. It crystallises from alcohol in bright yellow, lustrous needles, and melts at 207—208°. The *hydrochloride* melts and intumesces at 200°, and the *aurochloride* contains $2\text{H}_2\text{O}$ and melts at 220°.

The *azimide* of β -orthamidophenylmetatolimidazole,

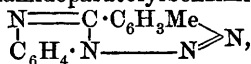


crystallises in yellow needles and melts at 187—188°.

β -Orthohydroxyphenylmetatolimidazole, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \nwarrow \text{N} \\ \nearrow \text{N} \end{array} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$,

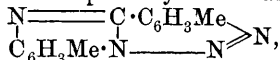
is obtained by hydrolysing the foregoing azimide with dilute sulphuric acid; it crystallises from alcohol in needles and melts at 241°.

The *azimide* of β -orthamidoparatolylbenzimidazole,



crystallises in yellow needles and melts at 185° ; exposure to sunlight renders it darker. The *platinochloride* crystallises in brown leaflets, softens at 275° , but is not melted at 290° .

The *azimide* of β -orthamidoparatolyltolimidazole,



crystallises in bright yellow needles and melts at 197° .

When the *azimide* of β -orthamidophenylbenzimidazole is dissolved in glacial acetic acid and treated with bromine (2 mols.), it yields the *dibromide*, $\text{C}_{13}\text{H}_8\text{N}_4\text{Br}_2$, which melts at 112° . There are also formed two isomeric monobromo-derivatives, the *monobromide*, $\text{C}_{13}\text{H}_7\text{N}_4\text{Br}$, which crystallises in pale orange needles and melts at 131 – 132° , and the more readily soluble *monobromide*, which crystallises in slender, dark yellow needles and melts at 146° .

The *azimide* of β -orthamidoparatolylbenzimidazole yields the *pentabromide*, $\text{C}_{14}\text{H}_7\text{N}_4\text{Br}_5$, which melts and decomposes at 120 – 130° ; ammonia converts it into the *dibromide*, $\text{C}_{14}\text{H}_8\text{N}_4\text{Br}_2$, which crystallises from glacial acetic acid in straw-yellow leaflets, and melts at 257° .

The *azimide* of β -orthamidoparatolylmetatolimidazole yields the *pentabromide*, $\text{C}_{15}\text{H}_{11}\text{N}_4\text{Br}_5$, which melts and decomposes at 155° ; the *monobromide* melts at 254° .

β -Naphthol- β -orthazobromophenylbenzimidazole, $\text{C}_{23}\text{H}_{15}\text{N}_4\text{OBr}$, crystallises in red needles and melts at 160 – 170° . The *hydrochloride* crystallises from glacial acetic acid, and melts and decomposes at about 252° ; the solution in concentrated sulphuric acid is deep cherry red.

The *hydrochloride* of β -naphthol- β -orthazoparatolylbenzimidazole forms a deep red, crystalline mass, and melts and decomposes at 276° .

β -Naphthol- β -orthazoparatolylmetatolimidazole has not been obtained in a condition free from β -naphthol; it melts at 147 – 150° .

M. O. F.

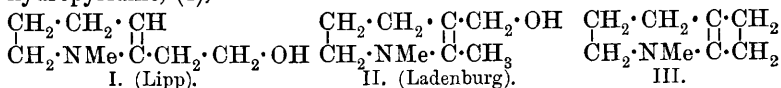
2-Methylidihydropyrroline, 1:2-Dimethylidihydropyrroline, and 1:2-Dimethylpyrrolidine. By R. HIELSCHER (*Ber.*, 1898, 31, 277–280).—2-Methylidihydropyrroline, $\text{NH} \begin{array}{l} \text{CMe} \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, obtained by

the action of alcoholic ammonia at 40 – 45° on methyl γ -bromopropyl ketone, boils at 50 – 51° under 110 – 116 mm. pressure, and has a sp. gr. = 0.8995 at 22° ; the *aurochloride* and *platinochloride* melt at 108° and 141 – 142° respectively; the hydrochloride is deliquescent. With methylamine instead of ammonia, reaction ensues at 0° ; the product, 1:2-dimethylidihydropyrroline, boils at 53 – 54° under 93 – 96 mm. pressure, and has sp. gr. = 0.9333 at 22° ; the *aurochloride* and *platinochloride* melt and decompose at 159° and 172 – 173° respectively. The base itself can be reduced by tin and hydrochloric acid to 1:2-dimethylpyrrolidine, which boils at 87 – 88.5° , and has a sp. gr. = 0.8299 at 20° ; the *aurochloride* melts at 179 – 180° , whilst the *platinochloride* was only obtained as a syrup.

C. F. B.

Isomerism in the Piperidine Series. By ALBERT LADENBURG (*Ber.*, 1898, 31, 286–289).—The compound obtained by Lipp (*Abstr.*, 1892, 1244, and *Annalen*, 289, 173) by allowing methylamine to react

with the bromide of acetobutylic alcohol and adding formaldehyde to the product, and formulated by him as 1-methyl-2-hydroxyethyl- Δ^2 -tetrahydropyridine, (I),



must rather have the constitution II. For when this compound is made to lose water, the product, which, presumably, has the constitution III, takes up 2 atoms of hydrogen, and then, when heated with hydrochloric acid, loses methyl and yields, not 2-, but 3-ethylpiperidine.

C. F. B.

2-Ethylpiperidine and its Methyl Derivative. By ALBERT LADENBURG (*Ber.*, 1898, 31, 290—291).—2-Ethylpiperidine has been prepared in a purer state than hitherto by the reduction, with sodium and alcohol, of 2-ethylpyridine which had been purified by repeated crystallisation of the mercurchloride (the aurochloride gives better results). It boils at 141—143°, and has a sp. gr. = 0.8666 at 0°; the hydrochloride melts at 178—181°, the platinochloride at 189°, decomposing at 191°, and the yellow *aurochloride*, previously obtained as an oil only, at 129—130°.

The methyl derivative was prepared by heating it with potassium methylic sulphate in aqueous alcoholic solution on the water bath, and removing unchanged secondary base in the form of its nitrosamine. It boils at 150—151.5°, and has a sp. gr. = 0.8515 at 0°; the *aurochloride* melts at 122—123°; the mercurchloride and deliquescent hydrochloride were also obtained crystallised, but not the platinochloride.

C. F. B.

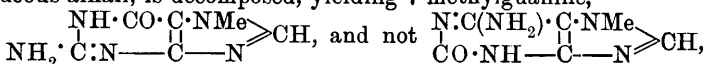
1-Methylpipercoline (1:2-Dimethylpiperidine). By ALBERT LADENBURG (*Ber.*, 1898, 31, 291—292).—This substance has been prepared by reducing picoline (2-methylpyridine) and methylating the product with potassium methylic sulphate, the unchanged secondary base being removed as the nitrosamine, and it has been compared with Lipp's 1-methylpipercolylalkine (*Abstr.*, 1892, 1244, and *Annalen*, 1895, 289, 226), obtained by acting with methylamine on acetobutylic alcohol, and reducing the product; the two substances are identical. The boiling point is 127.9° (corr.); the platinochloride, aurochloride, picrate, and stannochloride melt at 183—184°, 199—201°, 235—236°, and 129—130° respectively; the platinochloride of the methochloride melts and decomposes at 222°, and its *aurochloride* melts at 258°.

C. F. B.

Synthesis of Xanthine from Hydrogen Cyanide. By ARMAND GAUTIER (*Ber.*, 1898, 31, 449—450).—The substance formerly obtained by the author from hydrocyanic acid, and characterised by him as xanthine, shows a number of reactions, which are all given, not only by natural xanthine, but also by other members of the same group of compounds. In view of E. Fischer's statement (this vol., i, 214) that the compound obtained by him from hydrocyanic acid does not show the murexide reaction, and is therefore not identical with xanthine, the author proposes to reinvestigate the reaction, and

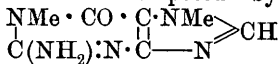
especially the other products which accompany the compound, which he has termed xanthine. A. H.

An Apparent Intramolecular Rearrangement in the Purine Group. By EMIL FISCHER (*Ber.*, 1898, 31, 542—545).—2-Chloro-6-amido-7-methylpurine (this vol., i, 280), when warmed with dilute aqueous alkali, is decomposed, yielding 7-methylguanaine,



an amido-oxy methylpurine, as would be expected if the reaction were a normal one. It was at first thought possible that a migration of the amido-group had taken place, but it has since been proved to be probable that the ring is first broken between N₁ and C₆ by the addition of the elements of a molecule of water, and then again closed by the elimination of a molecule of hydrogen chloride.

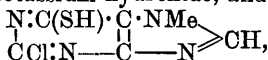
2-Chloro-6-methylamido-7-methylpurine is also decomposed by aqueous alkalis, yielding the dimethylguanaine,



(this vol., i, 98).

J. J. S.

Thiopurines. By EMIL FISCHER (*Ber.*, 1898, 31, 431—446).—When 2:6-dichloro-7-methylpurine is shaken for a quarter of an hour or so with normal potassium hydrosulphide solution in the cold, reaction takes place more readily than with potassium hydroxide, and the product is 2-chloro-6-thio-7-methylpurine,



which is formulated as containing the group :C(SH)· rather than ·CS·, because its methylic derivative (see below) readily yields methylic hydrosulphide when boiled with acids. This substance has no definite melting point; it is acid in character, like most of the substances described in the present paper, and forms many salts; it is oxidised by hydrochloric acid and potassium chlorate, or by alkaline hypobromites, but the product gives no murexide reaction; heating with strong hydrochloric acid displaces the Cl by OH, but removes some of the sulphur at the same time; reduction with hydriodic acid (sp. gr. = 1.96) and phosphonium iodide converts it into 6-thio-7-methylpurine, which crystallises with 1H₂O and melts when anhydrous at 310—311° (corr.). When this substance is shaken with methylic iodide and normal potash solution, it yields 6-methylthio-7-methylpurine, which melts at 212—213° (corr.) (in the case of the oxypurines, the methyl usually goes to the nitrogen atom); when it is heated with nitric acid of sp. gr. = 1.16, it is oxidised to 6-oxy-7-methylpurine. When 2-chloro-6-thio-7-methylpurine is heated with alcoholic sodium ethoxide at 100°, it forms 2-ethoxy-6-thio-7-methylpurine; this melts at 234° (corr.), forming a new substance, which then decomposes at 270—280°; heated on the water bath with hydrochloric acid of sp. gr. = 1.19, it yields 2-oxy-6-thio-7-methylpurine, which crystallises with 1H₂O, and melts and decomposes at 343° (corr.) when anhydrous.

When 2:6-dichloro-7-methylpurine is treated with excess of aqueous potassium hydrosulphide at 100° instead of at the ordinary tem-

perature, both chlorine atoms are removed, and 2:6-dithio-7-methylpurine, which has no definite melting point, is formed.

When 2:6:8-trichloro-7-methylpurine (1 mol.) is shaken for $2\frac{1}{2}$ hours with normal aqueous potassium hydrosulphide ($1\frac{1}{2}$ mols.), the product contains some dithiomethylpurine, but consists for the most part of monothio-compounds. On reducing it with hydriodic acid and phosphonium iodide, finally on the water bath, the hydriodide of 6-thio-7-methylpurine separates out first, accompanied by the hydriodide of the dithio-compound; these can be separated by decomposing the hydriodides with ammonia, evaporating, and extracting the residue with water, in which the monothio-compound is less soluble. The mother liquor from the hydriodides contains another thiomethylpurine, probably 8-thio-7-methylpurine, which melts at $248-249^{\circ}$ (corr.). Potassium hydrosulphide, then, attacks trichloro-7-methylpurine chiefly in the 6-position; with potassium hydroxide, it is almost entirely the 8-chlorine atom that is removed.

When trichloro-7-methylpurine is heated with excess of aqueous potassium hydrosulphide at 100° , the product is *trithio-7-methylpurine*, which is yellow, crystallises with $1\text{H}_2\text{O}$, and has no definite melting point.

By heating trichloropurine itself with a large excess of aqueous potassium hydrosulphide at 100° , *trithiopurine*, the sulphur analogue of uric acid, is obtained; this is yellow, and has no definite melting point.

Bromoxanthine, which will not react with potassium hydroxide, is converted by a large excess of aqueous potassium hydrosulphide at 120° into yellowish 2:6-dioxy-8-thiopurine; this crystallises with $1\text{H}_2\text{O}$, and, when heated, decomposes without melting.

C. F. B.

Diascorine, the Alkaloid obtained from the Tuber of *Dioscorea Hirsuta* Bl. By H. W. SCHÜTTE (*Chem. Centr.*, 1897, ii, 130—131; from *Ned. Tijdschr. Pharm.*, 9, 131—143).—Diascorine was discovered by Boorsma in the tuber of *Dioscorea hirsuta* Bl., which is known as “gadoeng” in Java. The alkaloid, which is extracted from the tuber by a solution of hydrogen chloride in alcohol, crystallises in yellowish-green plates, has a bitter taste, melts at 43.5° (uncorr.), is very hygroscopic, and easily soluble in water, alcohol, acetone, and chloroform, slightly in ether and benzene, and very slightly in light petroleum; it is a strong base, and slightly volatile in steam. With sulphuric acid and potassium iodate, it gives a brownish-yellow coloration which rapidly becomes bluish-violet; with sodium nitroprusside and an alkali, a reddish-violet coloration; and on warming with sulphuric acid, a reddish-violet. With mercuric chloride solution, it gives a white, amorphous precipitate, and with picric acid a yellow precipitate which melts at 184° ; with a solution of iodine in potassium iodide, it forms a white, amorphous precipitate, and with Bouchardat's reagent a brown precipitate, which gradually disappears. Phosphotungstic acid gives a white precipitate; phosphomolybdic acid, a yellowish-white; potassium cadmium iodide, a white; potassium bismuth iodide, a red, and bromine water a transient, yellow precipitate. The *hydro-*

chloride, $C_{13}H_{19}NO_2 \cdot HCl + 2H_2O$, crystallises from absolute alcohol in needles or plates, is very easily soluble in water, and has a specific rotatory power $[\alpha]_D = +4^\circ 40'$; the refractive index of a solution of 1.75 grams in 100 grams of water $n_D = 1.33776$. It loses its water of crystallisation at 100° , and the anhydrous salt melts at 204° (uncorr.). The *platinochloride* crystallises with $3H_2O$ in orange-yellow plates, and the anhydrous salt melts and intumesces at 199 – 200° . The *aurochloride* crystallises with $\frac{1}{2}H_2O$ in yellow needles, the anhydrous salt melting at 171° . Dioscorine has a weaker, but a similar, physiological effect to that of picrotoxin.

Boorsma's dioscorine and dioscorecine are identical, and dioscorine is the only poisonous base contained in the tuber. E. W. W.

Formulæ of Proteids and Composition and Nature of the Melanins. By OSWALD SCHMIEDEBERG (*Chem. Centr.*, 1897, i, 1062–1064; from *Arch. expt. Path. Pharm.*, 39, 1–84).—The dark brown to black pigments known as melanins are supposed to be either independent compounds like hæmoglobin, or derivatives of proteids, and the author, after examining a melanotic sarcoma, is inclined to the latter view. In order to readily compare the composition of these substances with that of other such compounds, he has calculated empirical formulæ from the various quoted analyses, with the following results. Fibrin, $C_{108}H_{162}N_{30}SO_{34}$; fibrinoglobulin, $C_{114}H_{176}N_{30}SO_{37}$; fibrinogen, $C_{111}H_{168}N_{30}SO_{35}$; paraglobulin from cows' or horses' blood, $C_{117}H_{182}N_{30}SO_{38} + \frac{1}{2}H_2O$; protofibrinose (protalbumose from fibrin), heterofibrinose, deutoalbumose from Witte's peptone, which the author names deuterofibrinose, the hemialbumoses (with varying amounts of water of crystallisation according to Kühne and Chittenden's analyses), $C_{102}H_{150}N_{30}SO_{31}$; dysofibrinose, $C_{105}H_{156}N_{30}SO_{33} + 4H_2O$; amphopeptone, $C_{108}H_{178}N_{30}SO_{43}$; antipeptone, $C_{108}H_{178}N_{30}SO_{43} + 1\frac{1}{2}H_2O$ (the author attributes the varying composition of the different preparations to the existence of several antipeptones, which differ from one another in the number of leucine or tyrosine molecules they have lost); Kühne and Chittenden's albumoses from paraglobulin—protalbumose, $C_{111}H_{176}N_{30}SO_{38} + \frac{1}{2}H_2O$; heteroalbumose, $C_{114}H_{176}N_{30}SO_{38} + \frac{1}{2}H_2O$; deutoalbumose, $C_{111}H_{176}N_{30}SO_{38} + H_2O$; Kühne's myosin, $C_{108}H_{172}N_{30}SO_{33}$; myoglobulin, $C_{114}H_{174}N_{30}SO_{36} + \frac{1}{2}H_2O$; protalbumose from myosin, $C_{108}H_{174}N_{30}SO_{34}$; deutoalbumose from myosin, $C_{105}H_{178}N_{30}SO_{36}$;

serum albumin from horses' blood, $C_{78}H_{122}N_{20}SO_{24}$; egg-albumin, $C_{80}H_{122}N_{20}SO_{24} + H_2O$; Kühne's antialbumide, $C_{120}H_{187}N_{27}SO_{37}$; hemipeptone obtained from serum albumin by boiling with 0.5 per cent. sulphuric acid, $C_{111}H_{176}N_{30}SO_{44} + \frac{1}{2}H_2O$; Lieberkuhn's deamidoalbuminic acid, $C_{160}H_{239}N_{27}S_2O_{65}$; Maly's oxyprotosulphonic acid, $C_{80}H_{122}N_{20}SO_{27} + 2\frac{1}{2}H_2O$.

Melanoidic acid, $C_{240}H_{239}N_{17}S_2O_{58}$, is prepared from serum albumin, purified by Hofmeister's method with ammonium sulphate, by coagulating and then digesting with dilute hydrochloric acid. It is a black, friable mass, and is only very slightly soluble in potassium hydroxide solution.

To prepare the melanin, the swellings from a large sarcomatous liver were macerated, washed with water, filtered, the fats then removed by

alcohol and ether, and the residue finally digested with pepsin-hydrochloric acid. The pigment grains remained undissolved, and were purified by warming with very dilute potassium hydroxide solution at 50–60° and filtering. The grains which pass through the paper were washed and dried in a centrifugal machine. Neglecting the 2·7 per cent. of iron which the melanin contained, its composition corresponded with the formula $C_{68}H_{72}N_{10}SO_{26} + \frac{1}{2}H_2O$.

Sarcomelaninic acid was prepared by digesting the pigment grains with dilute potassium hydroxide solution on the water bath for 2 or 3 days, and then precipitating with hydrochloric acid; this acid is not precipitated by acetic acid. Analyses of two preparations corresponded with the empirical formulæ $C_{68}H_{64}N_{10}SO_{26} + 2\frac{1}{2}H_2O$ and $C_{68}H_{67}N_{13}SO_{26} + 3\frac{1}{2}H_2O$ respectively.

The melanins hitherto prepared have very various compositions, thus the composition of Nencki's hippomelanin, prepared from the melanotic sarcomata of a horse, corresponds with the formula $C_{52}H_{39}N_9SO_{18} + \frac{1}{2}H_2O$, his phymatorhusin from human spleen and liver sarcomata with $C_{24}H_{20}N_4S_2O_7$, and Mörner's melanin with $C_{36}H_{43}N_7S_2O_7 + 1\frac{1}{2}H_2O$. Although in many cases the substances analysed were not homogeneous compounds, still the author maintains that this difference in composition is due to the different manner of their origin from proteids.

E. W. W

Prevention of the Precipitation of certain Proteids by Metallic Silver. By H. SCHADEE VAN DER DOES (*Zeit. physiol. Chem.*, 1898, 24, 351–353).—If fresh white of egg or blood-serum is shaken with freshly precipitated silver (0·05 grams to 10 c.c.) for a minute and then filtered, the filtrate is not coagulable by heat, neither are the globulins precipitated on dilution with water. The filtrate contains silver, and the silver on the filter paper contains something else, probably sulphur. The peculiarity in the behaviour of the proteid solutions may be due to the presence of silver in combination, or to the removal of something (? sulphur) from the proteid by the silver. The solutions resist putrefaction for a long time.

W. D. H.

[Decomposition of Albumin by Hydrochloric Acid]. By RUDOLF COHN (*Zeit. physiol. Chem.*, 1898, 24, 358–359).—Panzer (*ibid.*, 138) states that glutamic acid is obtainable in large quantities from the decomposition of proteid by hydrochloric acid. The present author states that he also has now found this to be the case, contrary to what he stated in his first contribution to the subject (*Abstr.*, 1896, i, 658).

W. D. H.

Preparation of a Carbohydrate from Egg-albumin. By JOHN G. SPENZER (*Zeit. physiol. Chem.*, 1898, 24, 354–357).—It is quite easy to prepare a carbohydrate from white of egg as Schützenberger, and, later, Pavy showed. The present paper states that this originates from the ovo-mucoid, and that if egg-albumin is obtained free from that substance it yields no carbohydrate at all.

W. D. H.

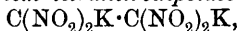
Urobilin. By GEORGES DENIGÉS (*Chem. Centr.*, 1897, i, 1128—1129; from *Bull. Soc. Pharm. Bordeaux*, 1897, März).—When ammonia is added to a solution of urobilin, its red colour changes to yellow and the absorption band in the blue portion of the spectrum disappears, but when a soluble zinc salt is added to the ammoniacal solution, this band reappears in a position nearer the red end of the spectrum and the solution shows a characteristic green fluorescence. The ammoniacal solution of urobilin gives a reddish coloration with mercuric sulphate, although the mixture is strongly alkaline, and nickel and copper salts give a violet coloration similar to that of the biuret reaction. Silver, ferric, ferrous and manganous salts (in presence of glycerol to avoid precipitation) and cadmium and magnesium salts have no effect. Thus the active salts are those which easily form double salts with ammonia or stable amine-like derivatives.

The presence of urobilin in highly coloured urines is difficult to detect by the spectroscope, especially when the colour is caused by bile pigments which absorb all the rays from yellow to violet, and although these colouring matters may be removed by lead or mercuric acetate, urobilin is also precipitated. The author finds, however, that when 5 c.c. of a solution of mercuric sulphate, prepared from 5 grams of mercuric oxide, 20 c.c. of sulphuric acid, and 100 c.c. of water is added to 10 c.c. of urine, the mixture allowed to remain five minutes and then filtered, the filtrate gives the spectroscopic test.

E. W. W.

Organic Chemistry.

Action of Potassium Cyanide on Bromopicrin. By ROLAND SCHOLL and MORDKO BRENNISEN (*Ber.*, 1898, 31, 642—653). When aqueous potassium cyanide is added to a well stirred alcoholic solution of bromopicrin, *symmetrical tetranitrodipotassioethane*,



is precipitated as a yellow, crystalline powder, which, when pure, forms dichroic yellow prisms and explodes at 270—275° or on percussion. When the aqueous solution is acidified with sulphuric acid, ether extracts from it an oil of characteristic odour, which, however, yields a white, and not a yellow, salt with potash. This substance is, therefore, not, as was expected, tetranitroethane; it is being more closely examined. The *silver* salt is a yellowish-red, crystalline precipitate. Tetranitropotassioethane is converted almost quantitatively, by the action of bromine, into *tribromotrinitroethane*, $\text{C}(\text{NO}_2)_2\text{Br}\cdot\text{C}(\text{NO}_2)_2\text{Br}_2$, which is a white, crystalline powder, and decomposes and melts when rapidly heated at 140°, when slowly heated, at 124—125°. It is decomposed when heated with water, a volatile oil and cyanogen bromide being formed, whereas it is not affected by boiling nitric acid. When it is distilled under a pressure of 50 mm., it yields three chief decomposition products, together with bromine and nitric oxide. The fraction of lowest boiling point consists of dibromodinitromethane, $\text{C}(\text{NO}_2)_2\text{Br}_2$, identical with that described by Losanitsch (*Abstr.*, 1884, 277). The second fraction, boiling at 108—110° under a pressure of 19 mm., consists of *tribromonitroethylene*, $\text{C}(\text{NO}_2)\text{Br}\cdot\text{CBr}_2$, which is a heavy, yellow oil with a penetrating odour; it unites with bromine to form a white, crystalline substance melting at 147°, probably *penta-bromonitroethane*, $\text{C}_2\text{Br}_5\cdot\text{NO}_2$. Finally, the residue left after the distillation of the tribromonitroethylene probably consists of *symmetrical dibromodinitroethylene*, $\text{C}(\text{NO}_2)\text{Br}\cdot\text{C}(\text{NO}_2)\text{Br}$, and crystallises in yellowish needles melting at 45°.

Tribromotrinitroethane is converted by aqueous potash into monobromodinitropotassiumethane, together with a small quantity of an oil smelling like bromopicrin, whilst potassium carbonate regenerates *symmetrical tetranitropotassioethane*.

These reactions show that tribromotrinitroethane has the constitution assigned to it above, from which that of the tetranitropotassioethane follows.

A. H.

An Impurity in Bromopicrin. By ROLAND SCHOLL and MORDKO BRENNISEN (*Ber.*, 1898, 31, 654—655). Compare the foregoing abstract).—When bromopicrin is slowly dropped into a well cooled and thoroughly agitated solution of 50 per cent. aqueous potash, and then saturated with carbonic anhydride, a yellow salt crystallises out; after recrystallisation from water, this forms lustrous, yellow crystals which consist of bromodinitropotassiumethane, $\text{C}(\text{NO}_2)_2\text{BrK}$, exploding at

155°. It is probably formed by the action of a trace of calcium nitrite on bromopicrin during the distillation of picric acid with calcium hypobromite. A. H.

Direct Nitration of the Paraffins. By R. A. WORSTALL (*Amer. Chem. J.*, 1898, 20, 202—217).—Konowaloff (Abstr., 1892, 575) has stated that, when normal hexane or octane is heated with nitric acid in sealed tubes at 130°, secondary nitro-compounds only are formed; the author finds, however, that primary compounds alone are produced by nitration in an open vessel.

When normal hexane is boiled with nitric acid (sp. gr. = 1·52 or 1·42), either alone or with concentrated sulphuric acid, during several days, a 60 per cent. yield of crude nitro-product is obtained; it consists of *primary nitrohexane*, $C_6H_{13}\cdot NO_2$, a light yellow oil which boils at 180—183°, is volatile with steam, and gives the nitrolic acid test; together with a *dinitrohexane*, probably primary, which has a light-yellow colour, is decomposed when distilled, and is sparingly soluble in aqueous alkalis, but readily in their alcoholic solutions, a red coloration being produced in both cases. On reducing nitrohexane, a *primary amine* is formed which gives the isonitrile and thiocarbimide reactions, and yields a *platinochloride*, $(C_6H_{13}\cdot NH_2)_2\cdot H_2PtCl_6$.

Normal heptane is more easily nitrated than normal hexane, a *primary nitroheptane*, $C_7H_{15}\cdot NO_2$, being formed, which boils at 193—196°, gives the nitrolic acid test, and is easily reduced to a *primary amine*. *Primary dinitroheptane*, $CH_3\cdot [CH_2]_5\cdot CH(NO_2)_2$, is a clear yellow oil, which is formed, together with nitroheptane, when the nitration is carried out with a mixture of nitric and sulphuric acids; it decomposes on being distilled, gives a red coloration with alkalis, and on reduction gives rise to ammonia and hydroxylamine, with, possibly, some heptoic acid.

A *primary nitro-octane*, apparently identical with that prepared by Eichler (Abstr., 1880, 229) from octylic iodide, is formed on heating normal octane with nitric acid (sp. gr. = 1·42), or with this and concentrated sulphuric acid; it boils at 205—210°, gives the nitrolic acid test, and is easily reduced to a *primary octylamine*, which gives the isonitrile and thiocarbimide reactions, and yields a *platinochloride*, $(C_8H_{17}NH_2)_2\cdot H_2PtCl_6$.

Fuming nitric acid (sp. gr. = 1·52) oxidises normal octane. *Primary dinitro-octane*, $CH_3\cdot [CH_2]_6\cdot CH(NO_2)_2$, is a clear yellow oil which closely resembles dinitrohexane and dinitroheptane; on reduction, it yields ammonia, hydroxylamine and octoic acid.

The products of oxidation by nitric acid of normal hexane, heptane, and octane, are invariably carbonic anhydride and acetic, succinic, and oxalic acids; the latter, however, is generally produced in very small quantity (0·04 per cent.), Schorlemmer stating that he was unable to detect its formation from hexane, octane, or diamyl. W. A. D.

Masut. By NICOLAI KROMER (*Zeit. anal. Chem.*, 1898, 37, 176—181).—The residue from the refining of Baku petroleum is much used in Russia as a fuel under the name of "masut"; the commercial article, however, frequently consists of imperfectly distilled crude oil, and numerous conflagrations have resulted from the

presence of hydrocarbons of low-boiling point. The examination of 100 samples showed that several of them had a flashing point as low as 47° , and one sample gave 82 per cent. of distillate below 310° .

The paper contains a tabular statement of all the results obtained.

M. J. S.

Synthesis and Constitution of Isoprene. By WILHELM EULER. (*J. pr. Chem.*, 1898, 57, 131—159).—A more detailed description of work on isoprene already published (see Abstr., 1897, i, 585).

A. W. C.

Ferrocyanides of Zinc and Manganese. By GEORGE C. STONE and D. A. VAN INGEN (*J. Amer. Chem. Soc.*, 1897, 19, 542—547. Compare Abstr., 1896, ii, 126 and 547).—Determinations of the ratio of iron to zinc in the precipitate formed on adding an excess of potassium ferrocyanide to a cold neutral solution of a zinc salt show that it has the composition $\text{Zn}_3\text{K}_2\text{FeC}_6\text{N}_6$; the precipitate obtained when the zinc is in excess has the same composition. Precipitation in cold solutions containing 5 per cent. by volume of hydrochloric acid gives a product $\text{Zn}_{10}\text{K}_8(\text{FeC}_6\text{N}_6)_7$; whilst from hot solutions, either acid or neutral, the compound $\text{Zn}_4\text{K}_4(\text{FeC}_6\text{N}_6)_3$ is obtained. The precipitate formed in solutions containing one-seventh per cent. by volume of hydrochloric acid had the composition $\text{Zn}_4\text{K}_4(\text{FeC}_6\text{N}_6)_3$, whilst a salt purchased as $\text{Zn}_2\text{FeC}_6\text{N}_6$ gave numbers corresponding to $\text{Zn}_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$.

From cold neutral solutions of manganese, the salt $\text{MnK}_2\text{FeC}_6\text{N}_6$ is precipitated on adding potassium ferrocyanide, when either the latter or the manganese is in excess. Precipitation from a cold solution containing 5 per cent. by volume of hydrochloric acid gives rise to the salt $\text{Mn}_4\text{K}_4(\text{FeC}_6\text{N}_6)_3$; whilst from hot solutions, whether neutral or acid, the compound $\text{MnK}_2\text{FeC}_6\text{N}_6$ is precipitated. The same salt is obtained from a cold solution containing one-seventh per cent. by volume of hydrochloric acid.

In the volumetric method of estimating zinc by potassium ferrocyanide, using an uranium salt as indicator on a porcelain plate, the end point corresponds with a salt of the composition $\text{Zn}_2\text{FeC}_6\text{N}_6$ when the solution contains one-seventh per cent. by volume of hydrochloric acid; when, however, the solution is hot and contains 10 per cent. of acid, it corresponds with the salt $\text{Zn}_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$. If the test be made on a filter-paper, so that the uranium does not come into contact with the precipitate, but only with the clear filtrate from it, the end point corresponds with the compound $\text{Zn}_4\text{K}_4(\text{FeC}_6\text{N}_6)_3$ when the solution is cold and contains one-seventh per cent. of hydrochloric acid; copper salts and ferric chloride, under identical conditions, indicate the same compound. A concentrated solution of cobalt when brought into contact, but not mixed with the zinc solution, also indicates $\text{Zn}_4\text{K}_4(\text{FeC}_6\text{N}_6)_3$, but very dilute cobalt solution, when mixed with the zinc solution, gives the reaction at a point corresponding with $\text{Zn}_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$. With cold solutions of manganese containing one-seventh per cent. by volume of hydrochloric acid, strong cobalt and uranium solutions on filter-paper indicate the formation of the

salt $\text{MnK}_2\text{FeC}_6\text{N}_6$, whilst with very dilute cobalt solution the end point corresponds with the compound $\text{Mn}_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$. The authors consider that cobalt is the most satisfactory indicator, since it develops a colour instantaneously, whilst the others do not. W. A. D.

Ferrocyanides of Zinc and Manganese. By EDMUND H. MILLER and JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1897, 19, 547—558. Compare Abstr., 1897, ii, 433, and preceding abstract).—The ferrocyanides of zinc and manganese, after being dried at 100° , still retain a considerable proportion of water, although probably not as water of crystallisation, as Wyruboff has stated (Abstr., 1877, ii, 19); it was determined by heating the salt in a current of dry air until it began to char, and absorbing the water formed, by calcium chloride. Zinc ferrocyanide precipitated from a cold, slightly acid solution of zinc chloride by potassium ferrocyanide, the zinc chloride being in excess, contains 9.37 per cent. H_2O , after being dried at 100° , whilst a determination of cyanogen, zinc, iron, and potassium in the completely dried salt, point to the composition of the latter being $\text{Zn}_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$. The ratio of zinc to iron in the salt precipitated by an excess of potassium ferrocyanide agrees with the formula $\text{Zn}_7\text{K}_6(\text{FeC}_6\text{N}_6)_5$.

Manganese ferrocyanide precipitated from a cold, slightly acid solution of manganous chloride, the latter being in excess, contains 3.23 per cent. H_2O after being dried at 100° , and appears to have the composition $9\text{MnK}_2\text{FeC}_6\text{N}_6 + \text{Mn}_2\text{FeC}_6\text{N}_6$, rather than $5\text{Mn}_2\text{FeC}_6\text{N}_6 + 4\text{K}_4\text{FeC}_6\text{N}_6$ as given by Wyruboff. An excess of potassium ferrocyanide precipitates a salt of different composition, the ratio of zinc to manganese being that required by the formula $15\text{MnK}_2\text{FeC}_6\text{N}_6 + \text{Mn}_2\text{FeC}_6\text{N}_6$.

Since the composition of the ferrocyanides obtained with an excess of a zinc or manganese salt is different from that formed by an excess of potassium ferrocyanide, an explanation is afforded of the fact that all attempts to estimate zinc or manganese by adding an excess of potassium ferrocyanide and titrating back with potassium permanganate have failed. W. A. D.

Inversion of Saccharose by Water. By BOHUSLAV RAÝMAN and OTTOKAR SULČ (*Chem. Centr.*, 1897, ii, 476; from *Rozpravy česke akad.* 5, [Klasse 2], 33).—When a 20 per cent. aqueous solution of saccharose was boiled in a glass flask standing on gauze and fitted with a reflux condenser, the rotation sank from $+11.66^\circ$ to $+5.94^\circ$ (100 mm. tube); when heated on the water bath, it sank to $+6.82^\circ$, and by heating in a platinum flask standing on asbestos, it was reduced from $+13.25^\circ$ to -3.42° . The amount of inversion is less when the solution is heated under pressure at 100° than when boiled under atmospheric pressure. Levulose is largely decomposed at 105° , and at 120° yields formic acid, furfuraldehyde, carbonic anhydride, pyrolevulinic acid, and humus-like substances. Dextrose is only slightly decomposed at 120° , a reducing substance of less optical activity being formed, but it is almost completely decomposed at 180° . Saccharose is only inverted to a very small extent by the action of amido-acids at 100° , but to a large extent

when heated at 105° under pressure. The greater the molecular weight of the acid employed, the less the amount of inversion effected.

E. W. W.

Gentianose. By ÉMILE BOURQUELOT and L. NARDIN (*Compt. rend.*, 1898, 126, 280—281).—Fresh gentian roots are cut into thin slices and added gradually to alcohol of 95° previously heated to boiling, the boiling being continued in a reflux apparatus for 20 to 25 minutes; any ferment present in the root is thus destroyed. The liquid is filtered, distilled, the residue neutralised with calcium carbonate, again filtered, and finally evaporated to a very thick syrup. After remaining at the ordinary temperature for some weeks, the semi-crystalline mass is dissolved in the smallest possible quantity of hot water, and 4.5 parts of hot alcohol of 95° is added for every 1 part of water, after which the liquid is allowed to remain at the ordinary temperature for 15 hours; the clear solution is then decanted off into another vessel, in which it gradually crystallises. The compound is purified by re-crystallisation from alcohol of 95° .

The gentianose thus obtained, forms anhydrous lamellæ which burn without residue, and are completely soluble in water, yielding colourless solutions. It melts at $207\text{--}209^{\circ}$, and is dextrogyrate; $[\alpha]_D = +31.25^{\circ}$, and no phenomenon of birotation could be recognised. Gentianose does not reduce cupric salts in presence of potassium hydroxide, but if boiled with dilute sulphuric acid, it becomes lævogyrate and acquires considerable reducing power. C. H. B.

Synthesis of Nitrogenous Compounds by means of Nitric Oxide. By WILHELM TRAUBE (*Annalen*, 1898, 300, 81—128).—In several papers recently published, the author has shown that, under suitable conditions, nitric oxide unites with a large number of organic compounds. The power of combining with nitric oxide is exhibited by all those compounds which yield isonitroso-derivatives under the influence of nitrous acid, namely, ethylic acetoacetate, ethylic malonate, and its alkylic derivatives, ethylic acetylsuccinate, nitroparaffins, ketones having a methenyl, methylene, or methyl group adjacent to the carbonyl radicle, diketones, ethylic phenylacetate, benzylic cyanide, resorcinol, phloroglucinol, ethylic succinylsuccinate, menthone, carvone, and similar compounds. Combination of these substances with nitric oxide, however, occurs only in presence of alkalis.

The "nitric oxide reaction," as the author refers to this method of synthesis, involves the replacement of hydrogen by the group N_2O_2H . In order to distinguish the compounds obtained by this means from the nitramines of Franchimont, they are called isonitramines (compare Hantzsch, this vol., i, 247). They are identical with the products of the action of nitrous acid on substituted hydroxylamines, and are also obtained by the hydrolysis of von Baeyer's bisnitrosyl compounds with hydrochloric or sulphuric acid.

Nitroethylisonitramine, $NO_2 \cdot CHMe \cdot N_2O_2H$, is obtained by the action of nitric oxide on the sodium derivative of nitro-ethane suspended in an alcoholic solution of sodium ethoxide (1 mol.). The *sodium* derivative is hygroscopic, but the solution yields crystalline derivatives with certain metallic salts; lead acetate gives a colourless precipitate, copper

sulphate a green, and silver nitrate a colourless derivative, which rapidly becomes black. The *barium* derivative separates in small, colourless plates, and is almost insoluble in water; it explodes when heated, and, like the other derivatives, is decomposed by mineral acids, yielding nitric oxide and ethylnitrolic acid.

The sodium derivative obtained by the action of nitric oxide on sodium nitromethane has not been obtained in the purified state; it is hygroscopic, and explodes with violence when heated.

Nitropropylisonitramine, $\text{NO}_2 \cdot \text{CHEt} \cdot \text{N}_2\text{O}_2\text{H}$, is prepared from nitropropane. The *sodium* derivative is not hygroscopic, and separates in slender needles on adding alcohol to the aqueous solution; it contains $\frac{1}{2}\text{H}_2\text{O}$, which cannot be removed without further decomposing the substance. Mineral acids eliminate nitric oxide, producing propylnitrolic acid. Metallic derivatives are precipitated from a solution of the sodium compound on adding metallic salts; all such derivatives explode with violence when heated.

Nitropentylisonitramine, $\text{C}_4\text{H}_9 \cdot \text{CH}(\text{NO}_2) \cdot \text{N}_2\text{O}_2\text{H}$, is obtained by the action of nitric oxide on nitropentane. The *sodium* derivative is hygroscopic, but the *barium* derivative is insoluble in water; the metallic derivatives explode less violently than those of the lower homologues.

Methylenedi-isonitramine, $\text{CH}_2(\text{N}_2\text{O}_2\text{H})_2$, arises from acetone, mesitylic oxide, methyl isopropyl ketone, acetophenone, and ethylic dimethylacetate on application of the nitric oxide reaction; it is most conveniently prepared from acetone (Abstr., 1895, i, 124). The *sodium* derivative contains $1\text{H}_2\text{O}$, and crystallises in the rhombic system; $a:b:c = 0.5832:1:0.3536$. The *lead* derivative is anhydrous, and the *potassium* derivative which dissolves with some difficulty in water, is insoluble in absolute alcohol; the *ammonium* derivative melts at 157° , and the *aniline* derivative is crystalline. The *dimethylic ether* occurs in two forms, the α -modification, which crystallises from alcohol and melts at 134° , and the β -modification, which dissolves more freely in alcohol, crystallises from water in intensely yellow leaflets, and melts at 74° ; the β -compound is decomposed by ammonia and alkalis, yielding nitrogen, nitrous oxide, and formaldehyde. The α -ether crystallises in the rhombic hemimorphic system; $a:b:c = 0.4550:1:1.0618$. The *diethylic ether* is also produced in two modifications. The α -ether crystallises from hot alcohol in colourless leaflets and melts at 82° ; it is indifferent towards mineral acids, but yields ammonia and hydrazine under the influence of sodium amalgam. The β -ether is an oil, and when treated with mineral acids yields colourless gas and formaldehyde.

Ethylidenedi-isonitramine, $\text{CHMe}(\text{N}_2\text{O}_2\text{H})_2$, is produced from diethyl ketone and from methyl ethyl ketone; the *lead* derivative is anhydrous, and crystallises in small cubes. The *dimethylic ether* melts at 75° , and crystallises in the rhombic system; $a:b:c = 0.4023:1:0.5641$. Free ethylidenedi-isonitramine is resolved by mineral acids into acetaldehyde and hydroxylamine, with elimination of oxides of nitrogen; sodium amalgam gives rise to hydrazine.

Propylidenedi-isonitramine, $\text{CHEt}(\text{N}_2\text{O}_2\text{H})_2$, forms a *lead* derivative which is anhydrous. The *dimethylic ether* melts at 56° , and crystallises in the monoclinic system; $a:b:c = 0.3064:1:0.3845$. $\beta = 103^\circ 5'$.

Benzylidenedi-isonitramine, $\text{CHPh}(\text{N}_2\text{O}_2\text{H})_2$, is prepared from methyl benzyl ketone, and from ethylic phenylacetate; the *sodium* derivative is hygroscopic, and the *barium* derivative is a colourless, crystalline powder. The *dimethylic ether* melts at 152° , and crystallises in the rhombic system; $a : b : c = 0.5413 : 1 : 1.1762$. The *diethylic ether* melts at 133° .

Isonitraminobenzoylacetone, $\text{COPh} \cdot \text{CHAc} \cdot \text{N}_2\text{O}_2\text{H}$, is obtained by the action of nitric oxide on benzoylacetone. The *sodium* derivative contains $1\text{H}_2\text{O}$, and separates in the form of a white, crystalline powder on adding alcohol to the aqueous solution; it is not hygroscopic, and the aqueous solution gradually decomposes spontaneously, yielding gas.

Di-isonitraminobenzyllic cyanide, $\text{CN} \cdot \text{CPh}(\text{N}_2\text{O}_2\text{H})_2$, is prepared from benzylic cyanide; the *sodium* derivative is a white, crystalline powder, and is not hygroscopic. The *barium* derivative is anhydrous, and dissolves with great difficulty in water. M. O. F.

Reactions of Phospham. By RAYMOND VIDAL (*Chem. Centr.*, 1897, ii, 517; from *Mon. Scient.*, [iv], 11, ii, 571).—A 90 per cent. yield of phospham is obtained by heating ammonium chloride with phosphorus pentasulphide in theoretical proportions. When phospham is heated with an alkali carbonate, phosphate, R_2HPO_4 , and cyanate are formed; by adding carbon, a cyanide is obtained; with iron, a ferrocyanide, and with sulphur, a thiocyanate. When heated with oxalates, phospham yields a phosphate and cyanogen; with methylic or ethylic alcohol, it reacts in accordance with the equations: $\text{PN}_2\text{H} + 4\text{ROH} = \text{OH} \cdot \text{PO}(\text{ONH}_2\text{R})_2$; $\text{OH} \cdot \text{PO}(\text{ONH}_2\text{R})_2 = \text{PO}_3\text{NH}_3\text{R} + \text{ROH} + \text{NHR}$; with propylic alcohol, the action is complex, propylamine and propylic oxide being formed. Diphenylamine is obtained when phospham is heated with phenol, and on boiling ethylenic glycol with phospham, ammonium hydrogen phosphate and acetylene are formed.

E. W. W.

Hexalkyldiarsonium Compounds. By ALFRED PARTHEIL and E. AMORT (*Ber.*, 1898, 31, 596—598).—By heating mercury arsenide, As_2Hg_3 (this vol., ii, 334), with an alkyl iodide in a sealed tube at 180° , a hexalkyldiarsonium mercuriodide, $\text{As}_2\text{R}_6\text{I}_2 + 2\text{HgI}_2$, is obtained. Silver chloride converts this into a compound of the hexalkylarsonium iodide with mercuric chloride; silver hydroxide, into the hexalkyldiarsonium hydroxide, from which the salts can be prepared by neutralisation with acids. The hydroxides themselves cannot be isolated; the propyl compound is decomposed when distilled, even under diminished pressure, and propylcacodylic acid is found in the distillate. The substances prepared are enumerated below with their melting points.

Hexamethyldiarsonium compounds: mercuriodide, yellow, 184° ; iodide, 171° with decomposition; mercurchloride, 211° ; platinochloride, yellow, unmelted at 255° .

Hexethyldiarsonium compounds: mercuriodide, yellow, 112° ; iodide, 162° with decomposition; chloride; mercurchloride, 137° ; platinochloride, yellow, 237° .

Hexapropyldiarsonium compounds: mercuriodide, yellow, 120° ; iodide, 150° with decomposition; compound of the latter with

mercuric chloride; *mercurochloride*, 169°; *platinochloride*, reddish-yellow, 189°.

Hexisopropyldiarsonium compounds: *mercuriodide*, yellowish-white, 114°; *iodide*, 150° with decomposition; *mercurochloride*, 171°; *platinochloride*, yellow, 211°.

Hexabutyldiarsonium compounds: *mercuriodide*, yellow, 109°; *iodide*, 145° with decomposition; *platinochloride*, yellow, 147°.

C. F. B.

Preparation of Acetone Oil and Methyl Ethyl Ketone from Suint. By A. BUISINE and P. BUISINE (*Compt. rend.*, 1898, 126, 351—353).—The fatty acids obtained from the water used for the desuintage of wool (this vol., i, 175) is neutralised with lime, evaporated to dryness, and the product distilled. It yields 45 to 50 per cent. of its weight of acetone oil of sp. gr. = 0·838, 80 per cent. of which is soluble in water. When fractionated, this oil yields 60 per cent. of methyl ethyl ketone, a compound hitherto difficult to obtain in any considerable quantity. This acetone oil is very suitable for the "denaturation" of alcohol, and since methyl ethyl ketone has almost the same boiling point as alcohol, the separation of the two is very difficult.

C. H. B.

Electrolysis of the Alkali Salts of Organic Acids. By JULIUS PETERSEN (*Chem. Centr.*, 1897, ii, 518—520; from *Bull. Acad. roy. Danemark*, 1897, 397—432).—From the results obtained by previous investigators, supplemented by his own work on the electrolysis of acid solutions of the potassium salts of acetic acid and its homologues, the author represents the decomposition as taking place in accordance with the following equations:—

- (1) $2C_nH_{2n+1} \cdot CO_2H = 2C_nH_{2n+1} \cdot CO_2 + H_2$.
- (2) $2C_nH_{2n+1} \cdot CO_2 + H_2O = 2C_nH_{2n+1} \cdot CO_2H + O$.
- (3) $2C_nH_{2n+1} \cdot CO_2 = C_{2n}H_{4n+2} + 2CO_2$.
- (4) $2C_nH_{2n+1} \cdot CO_2 = C_nH_{2n+1} \cdot CO_2 \cdot C_nH_{2n+1} + CO_2$.
- (5) $2C_nH_{2n+1} \cdot CO_2 + O = 2C_nH_{2n} + H_2O + 2CO_2$.

When a dilute acid solution of sodium formate is electrolysed, as the current intensity increases the amount of carbonic anhydride formed by oxidation of the acid decreases, but, in a concentrated solution, variation of current intensity has little effect on this action. As the concentration of the solution is diminished, more oxygen and less carbonic anhydride are liberated.

The end products of the electrolysis of these acids are those of (3), (4), and (5). Acetic acid is decomposed mainly in accordance with (3) and (1); in this case, the formation of methylic acetate was confirmed. Propionic, normal butyric, and isobutyric acids are decomposed for the most part according to (5), and (4) becomes more important as (3) diminishes. In the case of propionic acid, ethylic propionate was found amongst the products of electrolysis. The quantity of butane liberated varied directly, and the quantity of oxygen inversely, with the current intensity and the concentration of the solution. A solution containing 14 per cent. of the salt gave the maximum yield

of ethylene. Butyric acid yields propylic and isopropylic butyrates. More hexane and propylene and less hydrogen are liberated when the current intensity or the concentration of the solution is increased. Isobutyric acid yields di-isopropyl and isopropylic butyrate. Variations of current intensity or concentration of the solution have the same effect as in the preceding case, but the amount of di-isopropyl formed is less than the amount of hexane obtained from the normal acid under like conditions.

When oxalic acid is electrolysed, the current intensity has no effect on the nature of the products, but as the solution is diluted the amount of oxygen liberated increases. Malonic acid yields a small quantity of ethylene; the amount of carbonic oxide increases slightly with current intensity but much more with the concentration of the solution. An acid solution of potassium succinate gives neither carbonic oxide nor acetylene. The amount of ethylene liberated, however, increases with the current intensity and the concentration of the solution much more than in the case of any other acid; a 0.5 per cent. solution of the salt with 1.5 ampères at 0° gave 0.25 per cent. of ethylene in the gas obtained, and a 40 per cent. solution, 23.7 per cent. of this gas. Isosuccinic acid yields, not only oxygen, hydrogen, carbonic anhydride, and carbonic oxide, but also traces of ethylene and acetaldehyde. Less oxygen is liberated than in the case of succinic acid, some of the oxygen being used for the formation of acetaldehyde. The amount of ethylene and of acetaldehyde both vary directly with the current intensity and the concentration of the solution. Phenylacetic acid yields small quantities of benzaldehyde and benzoylphenylic acetate in addition to oxygen, hydrogen, and carbonic anhydride.

E. W. W.

Condensation Products of Aldehydes. Part III. Octoglycol Isobutyrate from Isobutaldehyde. By MAXIMILIAN BRAUCHBAR and LEOPOLD KOHN (*Monatsh.*, 1898, 19, 16—55. Compare Fossek, *Abstr.*, 1884, 37).—When isobutaldehyde is heated with sodium acetate in sealed tubes, *octoglycol isobutyrate* is obtained boiling at 138° under a pressure of 18 mm., or 250—252° at atmospheric pressure. The first step in the reaction is the production of an intermediate aldol condensation product, $\text{OH}\cdot\text{CHPr}^\beta\cdot\text{COPr}^\beta$, which then combines with a third molecule of the aldehyde in the following manner, $\text{OH}\cdot\text{CHPr}^\beta\cdot\text{COPr}^\beta + \text{CHPr}^\beta\text{O} = \text{OH}\cdot\text{CHPr}^\beta\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{COPr}^\beta$.

Octoglycol isobutyrate is a colourless oil of pleasant odour and bitter acid taste; it does not solidify on cooling, has a sp. gr. = 0.9438 at 15.7°/15.7° and molecular weight agreeing with the formula $(\text{C}_4\text{H}_8\text{O})_3$, and not with $(\text{C}_4\text{H}_8\text{O})_2$, as stated by Fossek. When treated with alcoholic potash, it is decomposed into octoglycol and isobutyric acid. It does not react with hydroxylamine, cannot be reduced, and is not altered on heating at 260° for 6 hours, which facts prove the non-existence of a carbonyl group in the substance.

On acetylation, it yields a *monacetyl* derivative differing but slightly in odour from the original substance, and boiling at 136° under a pressure of 17 mm. When heated in sealed tubes with sulphuric acid, it is converted into isobutyric acid and the oxides of octoglycol.

When octoglycol isobutyrate is oxidised with potassium permanganate, there are obtained, besides isobutyric acid and an oxy-acid, $C_8H_{16}O_9$, (a) a thick, colourless oil boiling at $156-160^\circ$ under a pressure of 17 mm., and still under investigation, (b) a colourless oil, $C_{12}H_{22}O_3$, boiling at 135° under a pressure of 17 mm., possessing a strong, although not unpleasant, odour; it contains no hydroxyl groups and on hydrolysis yields isobutyric acid and an oil smelling strongly of camphor; it is probably the isobutyrate of the ketone alcohol corresponding with octoglycol.

The authors have also prepared octoglycol isobutyrate by heating together pure octoglycol and isobutyric acid, and find that it has properties identical with the above.

A. W. C.

Alkylation of Isonitramino-derivatives of Fatty Acids. By WILHELM TRAUBE and HANS SIELAFF (*Annalen*, 1898, 300, 129—133).—The *methyl ether* of methylisonitraminoacetate, $COOMe \cdot CH_2 \cdot N_2O_2Me$, prepared by the action of methyl iodide on silver isonitraminoacetate, crystallises from alcohol in slender needles, and melts at 35° . The *amide* melts at 142° . Dilute hydrochloric acid resolves the ether into the *methyl ether* of isonitraminoacetic acid, $COOH \cdot CH_2 \cdot N_2O_2Me$; the *potassium* salt crystallises in lustrous leaflets, and explodes violently when heated.

The *ethyl ether* of isonitraminoacetic acid is crystalline, and the *benzyl ether* melts at 135° .

The methyl ether of isonitraminopropionic acid yields the *amide*, $COONH_2 \cdot CHMe \cdot N_2O_2Me$, which melts at 150° ; the corresponding *amide* derived from isonitraminobutyric acid melts at 126° . The *dimethyl ether* of isonitraminobenzylacetic acid,



melts at 82° .

M. O. F.

Isonitraminoisobutyric Acid and Nitrosobutyric Acid. By MOSES GOMBERG (*Annalen*, 1898, 300, 59—81. Compare Thiele and Heuser, *Abstr.*, 1896, i, 340).—*Dinitrosohydrazoisobutyric acid*, $N_2(NO)_2(CMe_2 \cdot COOH)_2$, produced by the action of nitrous acid on hydrazidoisobutyric acid, is a bright yellow, crystalline powder, which is very explosive in the dry state; it is fairly stable in presence of mineral acids, but is very sensitive towards alkalis, which liberate nitrogen from the substance. The nitrosamine explodes violently at $47-48^\circ$.

Isonitraminoisobutyric acid, $COOH \cdot CMe_2 \cdot N(NO) \cdot OH$, is obtained by decomposing the nitrosamine with sodium phosphate or sodium borate, which eliminate nitrogen, adding a smaller quantity of hydrochloric acid than corresponds with the sodium present, and then extracting with ether; it separates from a mixture of ether and petroleum in large, transparent crystals, and melts at $94-95^\circ$. Hydroxyisobutyric acid is also produced in the change, and when alkalis are employed, is accompanied by the *compound*, $C_8H_{16}N_2O_7$, which crystallises from a mixture of ether and petroleum in long, white needles, and melts at $92-93^\circ$. Isonitraminoisobutyric acid crystallises in the rhombic system; $a : b : c = 0.61160 : 1 : 0.66712$. The *lead* salt crystallises in small, transparent prisms, and contains $1H_2O$; it undergoes no loss of

weight at 130° , and explodes at 160° . The *potassium* and *ammonium* salts are crystalline, and the *silver* salt is amorphous, becoming crystalline in the dark; from warm solutions, the silver salt separates in crystals.

Hydroxylaminoisobutyric acid, $\text{COOH}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{OH}$, is produced by the action of hydrochloric acid on isonitraminoisobutyric acid. It crystallises from hot water in two forms, large, regular rhombohedra, melting and decomposing at 195 — 196° , and long white prisms, which do not melt at 260° ; recrystallisation from water frequently converts the former into the latter modification (compare Münch, Abstr., 1896, i, 203). The substance reduces neutral and ammoniacal solutions of silver nitrate, and also Fehling's solution, in the cold; nitrous acid regenerates isonitraminoisobutyric acid.

Methylic nitrosoisobutyrate, $\text{COOMe}\cdot\text{CMe}_2\cdot\text{NO}$, is obtained by the action of nitrous acid on methylic hydrazidoisobutyrate; it is a yellow oil which becomes emerald green when warmed, this colour disappearing as the liquid cools. It decomposes at 80 — 90° , and gives Liebermann's reaction; it reduces permanganate, but is indifferent towards ammoniacal silver and Fehling's solutions. A *polymeride* is formed along with the salt, and crystallises from a mixture of ether and petroleum; it melts at 105° . *Ethylic nitrosoisobutyrate* resembles the methylic salt.

M. O. F.

The Tautomeric Forms of Ethylic Acetoacetate and similar Compounds. By ROBERT SCHIFF (*Ber.*, 1898, 31, 601—609. Compare this vol., i, 237).—The enolic form of the compound of ethylic acetoacetate with benzylideneaniline is converted into the ketonic form by the action of a trace of piperidine, whilst the inverse change is brought about by traces of sodium ethoxide.

The ethylic acetoacetate of commerce varies in constitution according to the care which has been exercised in its preparation. Since it is made in presence of sodium ethoxide, the pure product should be the enolic form, and this was found to be the case in one sample (prepared by Kahlbaum), whilst all the other samples consisted of a mixture of the ketonic and enolic forms.

It has been hitherto found impossible to isolate the ketonic form of free ethylic acetoacetate, since the product, obtained by treating the enolic form with piperidine and distilling, is a mixture of both varieties. The coloration with ferric chloride is conditioned by the presence of the hydroxyl group, but the intensity of the coloration depends, not only on the proportion of the enolic form which is present, but also on the nature of the solvent, and especially on the presence of moisture, in the absence of which only a very slight coloration is produced.

The isomeric benzylideneaniline compounds of ethylic acetoacetate are all decomposed by a trace of sodium methoxide in presence of alcohol in a similar manner. The enolic form yields aniline and the enolic form of *ethylic phenylcarbinol-acetoacetate*,



which crystallises in white, silky needles, melts at $149\cdot5$ — 150° , and

gives a reddish-violet coloration with ferric chloride. The keto-compound, when treated in the same way, yields an isomeric *product*, $\text{CMeO}\cdot\text{CH}(\text{CHPh}\cdot\text{OH})\cdot\text{COOEt}$, melting at $133\text{--}134^\circ$. Finally, a mixture of the two forms yields a product which melts at 120° . If during this reaction, the solution is warmed, or allowed to remain too long in contact with sodium methoxide, only the enolic form of highest melting point is produced. When warmed with acetic anhydride, all three isomerides yield the same *acetyl* derivative, which is probably the enolic form, $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CHPh}\cdot\text{OAc})\cdot\text{COOEt}$, and melts at $150\text{--}151^\circ$. The isomerism of these compounds is due to the position of the mobile hydrogen atom of the acetoacetic group, and not in any way to the presence of an asymmetric carbon atom in the benzylidene-aniline residue, for a substance like the benzylideneaniline compound of ethylic malonate, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}(\text{COOEt})_2$, can only be obtained in a single form.

Ethylic benzoylacetate combines with benzylideneaniline to form an additive *compound*, which separates in yellowish-white crystals melting at 101° ; these constitute the ketonic form, and give no coloration with ferric chloride. If sodium ethoxide is added to the mixture of ethylic benzoylacetate and benzylideneaniline, the isomeric *enolic form* is obtained, which melts at 122° and gives a deep red colour with ferric chloride. Ethylic benzylidenediaceoacetate, prepared in the presence of piperidine, gives no coloration with ferric chloride and is the ketonic form; the enolic form is obtained by dissolving in alcoholic sodium ethoxide and precipitating with hydrochloric acid in the cold, but cannot be dried without passing back into the original ketonic form. In alcohol solution, it gives a deep greenish-violet coloration with ferric chloride.

A. H.

New Compounds of the Cerite Metals. By ANDRÉ JOB (*Compt. rend.*, 1898, 126, 246—248).—When lanthanum oxalate is dissolved in hot, concentrated hydrochloric acid and the solution is allowed to cool, *lanthanum oxalochloride*, $\text{La}_2\text{Cl}_2(\text{C}_2\text{O}_4)_2 + 5\text{H}_2\text{O}$, separates in crystals which remain unaltered at 120° , but lose their water at 230° . When treated with boiling water, they are decomposed with formation of a soluble chloride and an insoluble oxalate. When the anhydrous salt is heated at a red heat, it loses no chlorine, but the residue has the composition of the oxychloride, $\text{La}_2\text{O}_2\text{Cl}_2$.

Cerium and didymium form analogous compounds, and oxalobromides and oxaloiodides can also be prepared. Oxalonitrates have been described by other observers.

The formation of these complex oxalates, and the retention of halogens in the residues obtained by heating them, may possibly explain the differences between the atomic weights as determined by different observers.

C. H. B.

Dibromosuccinic Acids. By WILHELM C. LOSSEN (*Annalen*, 1898, 300, 1—5. Compare Abstr., 1897, i, 16).—A solution of dibromosuccinic acid which has been neutralised with soda, potash, baryta, or lime, decomposes on boiling in accordance with the three equations already put forward (*loc. cit.*), no material influence on the course of

the change being directly attributable to the nature of the base ; the volume of water, however, with which the salts are boiled has a controlling influence on the progress of the decomposition.

It has been stated by Kekulé that a fourth equation must be recognised, namely, $C_4H_4Br_2O_4 + H_2O = HBr + C_4H_5BrO_3$, but the author has not succeeded in confirming this observation, having been unable to establish the existence of bromomalic acid. Kekulé's statement that the calcium tartrate, obtained from dibromosuccinates which have been boiled with water, contains $3H_2O$ is erroneous ; the product is invariably a mixture of mesotartaric and racemic acids. M. O. F.

Decomposition of Normal Dibromosuccinates with Water. By WILHELM C. LOSSEN and ERNST REISCH (*Annalen*, 1898, 300, 5—31. Compare foregoing abstract).—The authors have made a large number of observations regarding the behaviour of dibromosuccinates towards boiling water, which decomposes them according to the following equations.

- I. $C_4H_2Br_2O_4X_2 = XBr + C_4H_2BrO_4X.$
- II. $C_4H_2Br_2O_4X_2 + H_2O = 2XBr + 2CO_2 + C_2H_4O.$
- III. $C_4H_2Br_2O_4X_2 + 2H_2O = 2XBr + C_4H_6O_6.$

The following is a summary of the results.

1. The nature of the base employed has no influence on the course of the decomposition ; this conclusion is opposed to that of Kekulé, who stated that baryta favours the production of bromomaleic acid, whilst tartaric acid is the main product when lime is employed.
2. Under parallel conditions, isodibromosuccinic acid decomposes more rapidly than dibromosuccinic acid.
3. Less bromine is eliminated from dibromosuccinic than from isodibromosuccinic acid.
4. The change represented by equation II is undergone by isodibromosuccinic acid to a greater extent than by dibromosuccinic acid.
5. Using 100 parts of boiling water, tartaric acid is produced in greater quantity from dibromosuccinic than from isodibromosuccinic acid ; both acids yield approximately the same amount when the dilution is one-fifth as great, the quantity of tartaric acid arising from isodibromosuccinic acid being the same in both cases.
6. A preponderating amount of mesotartaric acid is obtained on boiling neutral dibromosuccinates with water, isodibromosuccinates yielding chiefly racemic acid. The change represented by equation II is favoured by the employment of 100 parts of boiling water, decomposition proceeding more in accordance with equation I when the dilution is one-fifth as great. Dibromosuccinates decompose more slowly than the isomerides.
8. Cold water also decomposes dibromosuccinic acid and its salts less rapidly than isodibromosuccinic acid and its salts.
9. The greater the degree of dilution, the slower is the elimination of bromine from dibromosuccinates. On the other hand, isodibromosuccinates lose bromine more rapidly in dilute than in concentrated solutions.
10. Calcium acetate accelerates elimination of bromine from the calcium salts.
11. Using 200 parts of water, bromine is removed more rapidly from dibromosuccinic acid than from sodium dibromosuccinate.
12. The converse is observed in the case of isodibromosuccinic acid and its sodium salt.

The behaviour of dibromosuccinic and isodibromosuccinic acids towards

water is not in agreement with the view expressed by J. Wislicenus, that the former corresponds to racemic, and the latter to mesotartaric acid.

M. O. F.

So-called Bromomalic Acid. By WILHELM C. LOSSEN and ERICH MENDTHAL (*Annalen*, 1898, 300, 31—39).—The authors cast doubt on the existence of bromomalic acid, which was claimed by Kekule on the following grounds. (1) When sodium dibromosuccinate is boiled with water, hydrogen sodium bromomaleate is produced, which, when dried at 100°, has the formula $C_4H_4BrO_5Na$. (2) Hydrogen sodium bromomaleate yields calcium tartrate when boiled with lime-water; bromomaleic acid does not behave in this way. (3) The sodium salt is converted into a lead salt which has the composition of lead bromomaleate, and has properties different from those of lead bromomaleate.

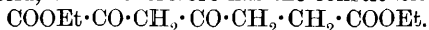
The authors give in detail their reasons for believing that the existence of bromomalic acid has yet to be proved.

M. O. F.

Hydrogen Sodium Bromomaleate from Dibromosuccinic Acid. By WILHELM C. LOSSEN and WALTHER RIEBENSAHM (*Annalen*, 1898, 300, 40—42. Compare foregoing abstract).—Under conditions apparently similar, hydrogen sodium bromomaleate separates from water in two forms, one containing $1H_2O$, the other being anhydrous. The authors have never obtained a salt which, after being dried at 100°, has the composition of hydrogen sodium bromomaleate.

M. O. F.

Constitution of Ethylic Oxalolevulinate (Ethylic Diketopimelate). By WILHELM WISLICENUS, KARL GOLDSTEIN, and MAX MÜNZESHEIMER (*Ber.*, 1898, 31, 622—626).—When ethylic oxalolevulinate is treated with aluminium amalgam and water, it is converted into *ethylic hydroxyketopimelate*, $C_{11}H_{18}O_6$, which is a yellowish oil boiling at 210° under a pressure of 16 mm. This substance is reduced by hydriodic acid at 200° to normal pimelic acid, the formation of which proves the presence of a normal chain of 7 carbon atoms in oxalolevulinic acid, which therefore has the constitution



The other reactions of oxalolevulinic acid and its ethylic salt all agree with this constitution. When the ethylic salt is distilled at the ordinary pressure, carbonic oxide is evolved and a distillate produced which boils at 105° under a pressure of 14 mm., but the reaction is by no means quantitative, and the product has not yet been obtained pure. It reacts with phenylhydrazine to form an unstable compound, which crystallises in plates and melts at 112°.

The pyrazole derivative of ethylic oxalolevulinate, on hydrolysis, yields a dicarboxylic acid melting at 165—167°, which loses carbon dioxide at 200° and is converted into 1-phenylpyrazolepropionic acid; this crystallises in long, colourless needles, melts at 120°, and boils at 235° under a pressure of 20 mm. The silver salt is a white, crystalline precipitate.

When ethylic oxalolevulinate is heated with 20 per cent. sulphuric acid, the free acid is obtained, but is very difficult to purify; it melts at 100—125° without decomposing, but when distilled decomposes into carbonic anhydride, carbonic oxide and levulinic acid. The acid

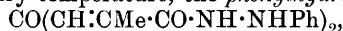
yields oxalic acid when heated with aqueous potash, and gives a red coloration with alcoholic ferric chloride. A. H.

Acetonedipyrvic Acid (Carbonyldimethylacrylic Acid). By OSCAR G. DOEBNER (*Ber.*, 1898, 31, 681—686.)—Pyruvic acid (90 grams) and acetone (45 grams) are dissolved in glacial acetic acid (120 grams), concentrated sulphuric acid (180 grams) is added, and the mixture heated at 105—110° for half an hour or until a portion poured into ice-cold water, and extracted with ether gives a crystalline product; the mass is then poured on to about 10 times its weight of ice and extracted with ether. A considerable quantity of *acetonedipyrvic anhydride*, $\text{CO} \begin{smallmatrix} \text{CH}:\text{CMe}\cdot\text{CO} \\ \text{CH}:\text{CMe}\cdot\text{CO} \end{smallmatrix} \text{O}$ or $\begin{smallmatrix} \text{CMe}:\text{CH} \\ \text{CO} \end{smallmatrix} \text{O} \begin{smallmatrix} \text{CH}:\text{CMe} \\ \text{O} \end{smallmatrix} \text{CO}$,

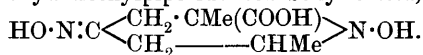
separates out, and a further quantity may be obtained from the ethereal solution; after several recrystallisations from alcohol, it is obtained in the form of square plates melting at 166° and distilling at 234° under a pressure of 20 mm. The yield is 7 to 8 grams. It is readily soluble in hot methylic or ethylic alcohol and in benzene, also in cold acetic acid, chloroform, or methylal, but insoluble in water or carbon bisulphide; it reduces both ammoniacal silver nitrate and alkaline copper solutions.

The *sodium* salt, $\text{C}_9\text{H}_8\text{O}_5\text{Na}_2 + 6\text{H}_2\text{O}$, is obtained when an alcoholic solution of the anhydride is mixed with the requisite quantity of sodium hydroxide solution and then evaporated until the salt begins to crystallise; the anhydrous salt is deliquescent. The *potassium* salt, $\text{C}_9\text{H}_8\text{O}_5\text{K}_2 + 2\text{H}_2\text{O}$, loses its water at 130°, and is not so deliquescent in the anhydrous form as the sodium salt. The *silver*, *copper*, and *ethyl*ic salts have been prepared; the last named is an oil.

When an aqueous solution of the potassium salt (1 mol.) and of phenylhydrazine hydrochloride (2 mols.) is allowed to remain for 12 hours at the ordinary temperature, the *phenylhydrazide*,



of the acid separates as an oil; it crystallises from hot alcohol in well-developed, orange-red prisms melting at 206°. The potassium salt of the acid, when warmed with hydroxylamine hydrochloride, yields large colourless crystals of the compound $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_4$ melting and decomposing at 209°; it has both acidic and basic properties, and is probably the oxime of N-hydroxydimethylpiperidonecarboxylic acid,



When the anhydride is heated with an excess of aqueous ammonia for 5 hours at 150°, a *dimide*, $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$, is obtained in the form of colourless, crystalline needles subliming at about 280° and decomposing above 300°; it dissolves in warm acids and is decomposed on heating with alkalis.

When the anhydride is reduced with sodium amalgam and alcohol, *acetonedipropionic anhydride* is obtained in the form of an oil.

The anhydride (2 grams) when heated in chloroform (24 grams) solution with bromine (5 grams) for 5 hours at 110° yields a *tetrabromide*, which, after recrystallisation from alcohol, melts at 178°.

J. J. S.

Formamide and its Sodium and Silver Salts. By PAUL C. FREER and P. L. SHERMAN, junr. (*Amer. Chem. J.*, 1898, 20, 223—228).—Formamide prepared by distilling ammonium formate under ordinary pressure is always contaminated with ammonium cyanide, formic acid, and ammonium formate; by heating ammonium formate, however, for 2 hours at 180° in an atmosphere of ammonia, and subsequently fractionating in the same atmosphere under $\frac{1}{2}$ mm. pressure, pure formamide can be prepared. It solidifies at -1° to a crystalline mass of needles, and has a sp. gr. = 1.16 at 4°; when heated above 100°, it is partially decomposed, the distillate between 203—216° containing water and ammonium cyanide.

Pure sodium formamide is quite stable at ordinary temperatures, but is rapidly decomposed by heat or moisture. *Silver formamide* is very sensitive to both light and heat.

The coloured silver compounds obtained by Titherley (*Trans.*, 1897, 460) from the sodium derivatives formed by the action of acid amides on sodamide, probably owed their colour to his sodium derivatives being contaminated by free sodamide; the authors have prepared colourless silver derivatives by the same method. The arguments of Titherley as to their structure are therefore valueless. W. A. D.

Conversion of Methylpyromucic Acid into Aldehydopyromucic and Dehydromucic Acids. By HENRY B. HILL and HARRIS E. SAWYER (*Amer. Chem. J.*, 1898, 20, 169—178).—On heating ω -bromomethylpyromucic acid (Hill and Jennings, *Abstr.*, 1893, i, 311), dissolved in chloroform, with an excess of bromine, ω -dibromomethylpyromucic acid is formed, but only in very small quantity; it crystallises from benzene in small, greenish-white prisms, melts at 153°, is easily soluble in ether and chloroform, but almost insoluble in light petroleum and carbon bisulphide, and is decomposed by alcohol or water, the solution obtained in the latter case showing aldehydic properties.

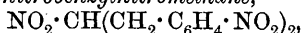
Methylpyromucic chloride, $C_6H_5O_2Cl$, prepared by the action of phosphorus pentachloride or trichloride on methylpyromucic acid, melts at 28° to a colourless liquid which boils at 93—94° under 18 mm. pressure, and at 202° under 756 mm. pressure. When heated with bromine ($2\frac{1}{2}$ mols.) in bright sunlight at 150°, it yields ω -dibromomethylpyromucic bromide, which crystallises from chloroform or benzene in elongated plates and melts at 102°; it is decomposed by boiling water into tetrabromomethane, and, in much larger quantity, *aldehydopyromucic acid*, $C_6H_4O_4$. The latter crystallises from hot water in irregular, curved plates which are anhydrous, and from cold water in long, slender needles, with $1H_2O$, which rapidly effloresce; it is easily soluble in alcohol, less readily in ether and chloroform, and very sparingly in benzene, light petroleum, or carbon bisulphide. When quickly heated, it melts at 201—202°, but when slowly heated it sublimes and decomposes, the residue melting above 202°. The *oxime*, $C_6H_5NO_4$, crystallises from boiling water, and, when rapidly heated, melts and decomposes at 224—226°. The *phenylhydrazone*, $C_{12}H_{10}N_2O_3$, melts and decomposes at 176°, and is easily soluble in alcohol, less easily in ether, and almost insoluble in benzene, chloroform, and carbon bisulphide.

Dehydromucic acid, identical with that obtained from mucic acid, is

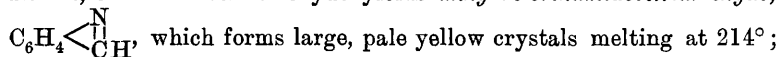
formed on oxidising a solution of aldehydopyromucic acid in dilute caustic soda with silver oxide; it was characterised by its barium salt.

W. A. D.

Condensation of Nitromethane with Substituted Aromatic Aldehydes. By THEODOR POSNER (*Ber.*, 1898, 31, 656—660).— ω -Orthodinitrostyrene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CH} \cdot \text{NO}_2$, is formed when ortho-nitrobenzaldehyde is heated with nitromethane and zinc chloride at 160° , and is identical with the compound obtained by Priebis (Abstr., 1885, 161) by the nitration of ω -nitrostyrene. It was found impossible to obtain any definite product by the reduction of this substance. Ortho-nitrobenzyl chloride is converted by nitromethane and sodium ethoxide into *di-ortho-nitrobenzyl nitromethane*,



which forms dark yellow crystals melting at 140 — 141.5° . The mono-substituted benzyl nitromethane could not be obtained. Metanitrobenzaldehyde also reacts with nitromethane in the presence of zinc chloride to form ω -metadinitrostyrene, identical with the product obtained by Friedländer and Lazarus from metanitrocinnamic acid and nitric acid (Abstr., 1885, 1138), but no analogous compound could be obtained from any other aromatic aldehyde. Under the same conditions, orthamidobenzaldehyde yields *anhydro-orthamidobenzaldehyde*,



this substance is not identical with the base to which Rudolph assigns the same constitution (Abstr., 1880, 469). With acetic anhydride,

it yields an *acetyl* derivative, $\text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{CAc} \end{array}$, which is a white, micro-crystalline powder melting at 210° . The molecular weight, as determined by the boiling point method in acetic acid, agrees with the above formula.

A. H.

Derivatives of Catechol. By JULIUS HESSE (*Ber.*, 1898, 31, 598—601).—Dichloroacetal does not react with phenol, resorcinol, quinol, hydroxyquinol, or pyrogallol, but it does react with catechol when it is heated with the disodium derivative of that substance for 16 hours at about 200° . The product, 1:2-phenylenediethylglyoxal, $\text{C}_6\text{H}_4 \cdot \text{O}_2 \cdot \text{CH} \cdot \text{CH}(\text{OEt})_2$, is a thick liquid which boils at 150° (uncorr.) under 22 mm. pressure, decomposes when distilled under atmospheric pressure, and has a sp. gr. = 1.1252 at 14° ; it forms a yellow *nitro*-derivative which melts and decomposes at 125° . When it is boiled for several hours with dilute sulphuric acid, and the alcohol and unchanged acetal are then distilled over with steam, 1:2':6'-trihydroxyhydro-cumarone, $\text{OH} \cdot \text{C}_6\text{H}_3 \cdot \text{C} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}(\text{OH}) \end{array} \text{CH}(\text{OH})$, crystallises out from the residual liquid, as the latter cools, in yellowish, monoclinic crystals [$a:b:c = 2.218:1:3.564$; $\beta = 120^\circ 14'$] which melt at 131° .

C. F. B.

3:4:5-Tribromaniline and Derivatives of Unsymmetrical Tribromobenzene. By C. LORING JACKSON and FRANK B. GALLIVAN (*Amer. Chem. J.*, 1898, 20, 179—189).—3:4:5-Tribromaniline, formed

on reducing the tribromonitrobenzene prepared by the diazo-reaction from dibromoparanitraniline, crystallises from dilute alcohol in slender, white needles and melts at $118-119^{\circ}$, whereas Körner (*Gazzetta*, 1874, 409) states that it decomposes above 130° without melting; it is converted by elimination of the amido-group into 1 : 2 : 3-tribromobenzene, and by the action of bromine into pentabromaniline. The *hydrochloride* crystallises from very dilute hydrochloric acid in white needles, but is partially decomposed on being boiled with water, although it is much more stable than 2 : 4 : 6-tribromaniline hydrochloride; the *hydrobromide* closely resembles the hydrochloride, whilst the *sulphate* crystallises from dilute sulphuric acid in white, lustrous plates. 3 : 4 : 5-Tribromophenylurethane, $C_6H_2Br_3 \cdot NH \cdot COOEt$, formed on heating ethylic chlorocarbonate dissolved in benzene with 3 : 4 : 5-tribromaniline, crystallises from dilute alcohol in white, rhombic plates, melts at $169-170^{\circ}$, and is converted into diphenylcarbamide when heated with aniline.

3 : 4 : 5-Tribromacetanilide crystallises from alcohol in white, globular aggregates of needles, melts at $253-254^{\circ}$, is soluble in benzene but nearly insoluble in ether, chloroform, and light petroleum, and is not easily hydrolysed by sulphuric acid; it is converted by cold nitric acid (sp. gr. = 1.50) into 3 : 4 : 5-tribromo-2-nitracetanilide, which separates from alcohol and acetone in well-formed crystals, is almost insoluble in benzene, ether, and light petroleum, and is converted by boiling alkalis into 3 : 4 : 5-tribromo-2-nitraniline. The latter crystallises from alcohol in orange-yellow needles, is easily soluble in ether, benzene, and chloroform, and melts at 130° ; on diazotising in alcohol acidified with sulphuric acid, and boiling, a tribromonitrophenol is formed which crystallises from alcohol and melts at 230° .

2 : 4 : 5-Tribromophenylurethane crystallises from dilute alcohol in long, slender needles, is easily soluble in benzene, chloroform, and glacial acetic acid, and melts at 101° ; when heated with aniline, it yields diphenylcarbamide.

On adding 2 : 4 : 5-tribromacetanilide (Abstr., 1895, i, 212) to nitric acid (sp. gr. = 1.50), a 2 : 4 : 5-tribromonitracetanilide is formed, which crystallises from alcohol in small, pinkish-white needles, melts at 228° , and is easily soluble in the ordinary solvents; by boiling dilute sulphuric acid (sp. gr. = 1.44), it is converted into the corresponding 2 : 4 : 5-tribromonitraniline, which crystallises from alcohol in stout, yellow needles, melts at 130° , and is easily soluble in the ordinary solvents.

The authors find that the substance formed by the action of sodium ethoxide on 1 : 2 : 4-tribromo-3 : 5-dinitrobenzene is not a tribromodithoxybenzene as formerly stated by them (Abstr., 1895, i, 212), but a tribromonitrophenetol; at the same time, a bromodinitroresorcinol is formed, which yields an orange-yellow barium salt, $C_6HBr(NO_2)_2Ba$, which is soluble in water and explodes when strongly heated.

W. A. D.

New Method for the Production of Acetyl Derivatives of Amido-compounds. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, 31, 661—663).—The acetyl derivatives of aromatic amido-compounds can

be prepared by the aid of thiacetic acid much more readily than by the ordinary method with acetic acid, the reaction proceeding at a much lower temperature and much more rapidly, whilst the yield is almost theoretical. The reaction has been applied to the preparation of acetanilide, metanitracetanilide, which melts at 154—156°, acetomethylanilide, asymmetrical acetylphenylhydrazine, diacetylbenzidine and acetylanthranilic acid, and in all cases with good results.

A. H.

Action of Primary, Secondary, and Tertiary Bases on Orthoxylylenic Bromide. By ALFRED PARTHEIL and TH. SCHUMACHER (*Ber.*, 1898, 31, 591—594).—The authors have been working on the same lines as Scholtz (this vol., i, 305), and have obtained substantially the same results, although frequently under somewhat different conditions, as, for instance, in alcoholic solution at 100°, instead of in chloroform solution at the ordinary temperature; the melting points observed differ slightly from those of Scholtz in many cases. The following compounds were not prepared by Scholtz; the numbers given are melting points.

2'-Paraphenetidinedihydroisindole, $C_8NH_8 \cdot C_6H_4 \cdot OEt$, 204—205°. *Xylylenedipiperidyl picrate*, 227° with decomposition. *Xylylenedimethylammonium bromide*, $C_6H_4(CH_2 \cdot NMe_3Br)_2$, 207—208°; *platinochloride*, with $\frac{1}{2}H_2O$, orange-red, 253°, with decomposition; *aurochloride*, yellow, 249—250°; *mercuriochloride*, 179—180°. With triethylamine in alcoholic solution, at 100°, xylylenic bromide yields *xylylenedimethylammonium bromide*, the *platinochloride* corresponding to which melts and decomposes at 237—238°; if the two substances are heated only until the bromide has just dissolved, the product is *xylylene-mono-triethylammonium bromide*, $CH_2Br \cdot C_6H_4 \cdot CH_2 \cdot NEt_3Br$, the *aurochloride* corresponding to which melts at 115—116°. C. F. B.

Hydramides and Isomeric Bases (Glyoxalidines). By MARCEL DELEPINE (*Compt. rend.*, 1898, 126, 343—346).

	Molecular heat of combustion.		Heat of formation from elements.
	Constant volume.	Constant pressure.	
Anisaldehyde, $C_8H_8O_2$	966·7 Cal.	967·3 Cal.	+ 63·1 Cal.
Anishydramide $(C_8H_8O)_3N_2$...	3040·8	3042·8	+ 48·4
Anisine, $C_{24}H_{24}N_2O_3$	3024·6	3026·6	+ 64·6
Furfuramide, $C_{15}H_{12}N_2O_3$	1827·87	1828·15	+ 0·35
Furfurine, $C_{15}H_{12}N_2O_3$	1810·32	1810·6	+ 17·9

Furfurine hydrochloride, $C_{15}H_{12}N_2O_3 \cdot HCl$.—Heat of dissolution, - 4·75 Cal. Heat of combination of solid furfurine with the dissolved acid, + 6·55 Cal.; with the gaseous acid, + 28·7 Cal.

It follows from the above results that the conversion of solid furfuramide into furfurine develops + 17·55 Cal., and the conversion of anishydramide into anisine develops + 16·2 Cal. Similar results have previously been obtained with hydrobenzamide and amarine. The thermal values explain why the isomerides of the hydramides cannot be reconverted into their generators by the action of acids, either strong or dilute.

C. H. B.

d d 2

Decomposition of Diazo-compounds: Reaction of Diazo-phenols and of the Salts of Chloro- and Bromo-diazobenzene with Ethylic and Methylic Alcohols. By FRANK K. CAMERON (*Amer. Chem. J.*, 1898, 20, 229—251).—Paradiazophenol chloride yields phenol only when heated with ethylic or methylic alcohol, either alone or in presence of gaseous hydrogen chloride, ammonia, or sulphurous anhydride, no sulphonic acid being formed in the latter case; phenol is also formed on decomposing the diazo-salt with either of the above alcohols containing 20 per cent. of sulphuric acid or potassium hydroxide. A solution of paradiazophenol chloride in ether is not acted on by sulphurous anhydride.

Orthodiazophenol chloride similarly yields phenol only when treated with methylic or ethylic alcohol, either alone or in presence of gaseous hydrogen chloride or sulphurous anhydride.

Metadiazophenol chloride, when decomposed by dilute hydrochloric acid, yields resorcinol only, and phenol only when heated with ethylic or methylic alcohol.

Both the nitrates and sulphates of orthochlorodiazobenzene and orthobromodiazobenzene give the hydrogen reaction only when heated with either ethylic or methylic alcohol, chlorobenzene and bromobenzene being obtained respectively. The salts of metachlorodiazobenzene and of metabromodiazobenzene give the hydrogen reaction only when heated with ethylic alcohol; methylic alcohol, however, effects the introduction of a methoxy-group, metachloranisole and metabromanisole being respectively formed, together with, in smaller quantity, chlorobenzene and bromobenzene.

Parachlorodiazobenzene nitrate, on being heated with ethylic alcohol, gives rise principally to chlorobenzene, a small quantity of parachlorophenetole and of 4:3-chloronitrophenol being also formed (compare Remsen and Orndorff, *Abstr.*, 1888, 268; Beeson, *Abstr.*, 1894, i, 329, and Chamberlain, *Abstr.*, 1897, i, 562); parachlorodiazobenzene sulphate yields chlorobenzene only under similar conditions, whilst parabromodiazobenzene salts give rise to bromobenzene.

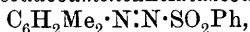
With methylic alcohol, parachlorodiazobenzene nitrate yields parachloranisole and a small quantity of 1:3:4-chloronitrophenol, no chlorobenzene being formed; parabromodiazobenzene nitrate gives rise to parabromanisole and 4:3-bromonitrophenol. The sulphates of parachlorodiazobenzene and parabromodiazobenzene produce respectively parachloranisole and parabromanisole only.

The following conclusions are drawn from this work and that of other authors. (1) That the alkyloxy-reaction is normal, whereas the hydrogen reaction is induced only by special conditions. (2) Regarding water as the first member of the series, the more complex the alcohol the greater is the tendency towards the hydrogen reaction. (3) The acid radicles, COOH, Cl, Br, NO₂, &c., especially when in the ortho-position, induce the hydrogen reaction (compare Remsen and Graham, *Abstr.*, 1889, 975), their relative influence being probably according to the order in which they are named; when in the meta-position, their influence is not so great, whilst in the para-position it is still less.

W. A. D.

Diazo-cyanides and the Reaction of Diazo-compounds with Benzenesulphinic Acid. By ARTHUR HANTZSCH (*Ber.*, 1898, 31, 636—642).—Syndiazocyanides are formed when potassium cyanide is added to an acid solution of a diazonium salt, whereas, as a rule, diazoimidocyanides are produced when the diazonium salt is brought into an alkaline solution of potassium cyanide. In some cases, however, if only one product is stable, this is formed when either of these methods is employed. This is the case with pseudocumene-diazocyanide melting at 38—39°, which can be preserved for some time at the winter temperature and has now been analysed. In other cases, the *syn*-diazocyanide is formed in the alkaline solution of potassium cyanide, and then, by contact with the solution, is converted into the diazoimidocyanide. Parabromodiazonium chloride acts in this way, the orange-red *syn*-diazocyanide being the first product, but changing in the course of 20 minutes into the brownish-yellow *parabromantidiazimidocyanide*, $C_6H_4Br \cdot N \cdot N \cdot C(NH) \cdot CN$, which melts at 109—110°. Similar observations have been made on the behaviour of parachlorodiazonium chloride, the *diazoido ether* of which melts at 103—105°. The *syn*-diazocyanides are also readily formed by the action of hydrocyanic acid on the diazo-oxides. Hydrochloric acid, on the other hand, reacts very slowly with these oxides and produces diazonium salts. The diazo-oxides react with potassium sulphite to form diazosulphonates, and with benzenesulphinic acid to produce diazosulphones. Thus parachlorodiazo-oxide is converted by hydrogen cyanide into parachloro*syn*diazocyanide, by potassium sulphite into parachloro-*syn*-diazosulphonate, and by benzenesulphinic acid into parachlorodiazo-phenylsulphone, which melts at 106—107°, and not at 102—103° as stated by Singer.

Most of the *syn*-diazocyanides combine with benzenesulphinic acid to form colourless additive compounds, from which the *anti*-cyanide is produced by removal of the acid. Pseudocumene*syn*diazocyanide, on the other hand, yields *pseudocumeneantidiazosulphone*,



melting at 84°. The *anti*-diazosulphones do not form colouring matters with free naphthol, but do so in presence of an alkali. Benzenesulphinic acid yields colourless additive products with azobenzene and most of the aromatic diazo-compounds of the azo-type, but does not react with azo-compounds of the fatty series. When a solution of diazonium hydroxide is neutralised with benzenesulphinic acid, the solution contains diazonium benzenesulphinate, which is isomeric with benzenediazosulphone. This solution behaves in all respects as one of a diazonium salt, and gradually yields nitrogen and phenol, free benzenesulphinic acid being left in solution.

Benzenesulphinic acid reacts in a remarkable manner with diazo-amido-compounds, forming a diazosulphone, which unites with 1 mol. of the acid, and a salt of the amine which contains the more negative radicle. Diazoamidobenzene yields aniline benzenesulphinate and the additive compound of benzenediazosulphone and benzenesulphinic acid melting at 175—176°. Parabromodiazoamidobenzene yields the *benzenesulphinate of parabromaniline*, and benzenediazosulphone; paranitrodiazoamidobenzene similarly yields *paranitraniline benzenesul-*

phinate, melting at 145—148°, and benzenediazosulphone. Paratoluenediazoamidobenzene, on the other hand, gives a mixture of the benzene-sulphinates of aniline and paratoluidine, so that where the two groups are not very distinct in electrochemical character, the compound appears to act as a tautomeric one. A. H.

Ethyllic Benzeneazocyanacetate. By HANS WEISSBACH (*J. pr. chem.*, 1898, 57, 206—207).—When carbonic anhydride is passed into a dilute alcoholic solution of the potassium derivative of ethylic benzeneazocyanacetate at ordinary temperatures, the β -modification, doubtless really a phenylhydrazone, $N_2HPh:C(CN)\cdot COOEt$, is obtained, whereas if the temperature is increased to 60°, a third (γ) isomeric substance is also formed, separating from light petroleum in well-formed, red crystals melting at 84°; if kept in a state of fusion for some time, it is converted into a substance melting at 118°, possibly yet a fourth isomeride. The chemical behaviour and red colour of the γ -modification point to its being an azo-compound, namely, the true *ethyllic benzeneazocyanacetate*, $CN\cdot CH(N_2Ph)\cdot COOEt$. It is not acted on by acetic chloride, whereas the corresponding α - and β -modifications are converted into a mixture of two isomeric *acetyl* derivatives, the one melting at 158° and the other at 166°. On hydrolysing with cold sodium hydroxide, both are converted into the same *acid*, $NPhAc\cdot N:C(CN)\cdot COOH$, forming small needles melting at 210°, and yielding an amide separating in yellow crystals. Further research on this subject is in progress. A. W. C.

Parahydroxyphenylhydrazine. By JULIUS ALTSCHUL (*J. pr. chem.*, 1898, 57, 201—204).—Philipp (*Abstr.*, 1893, i, 78) was unable to prepare parahydroxyphenylhydrazine by the V. Meyer-Lecco method, but the author finds that, by the action of alcoholic hydrogen chloride on potassium hydroxyphenylhydrazinesulphonate, *parahydroxyphenylhydrazine hydrochloride* is obtained, crystallising from water in colourless needles; it reduces Fehling's solution and ammoniacal silver nitrate in the cold. The *oxalate* crystallises in colourless leaflets. Attempts to prepare the free base have so far proved unsuccessful.

Nitrosoparahydroxyphenylhydrazine, formed by the action of nitrous acid on the hydrochloride, separates in small, brownish crystals and has the peculiar penetrating odour of nitrosophenylhydrazine. A. W. C.

Nitrosoalphenylhydroxylamines. By EUGEN BAMBERGER (*Ber.*, 1898, 31, 574—589).—When nitrosophenylhydroxylamine, $NO\cdot NPh\cdot OH$, is allowed to remain in benzene solution at 0° or at the ordinary temperature, it decomposes; gas is evolved, consisting chiefly of nitrogen, but containing also carbonic anhydride and a little nitric oxide; a solid deposit is gradually formed, which at first is mainly diazobenzene nitrate, but afterwards contains dipara- and orthopara-dinitrodiphenylamine, paranitrodiphenylamine, and in one case the nitrosamine of the last substance; the mother liquor is found to contain nitrosobenzene and phenol. The diparanitrodiphenylamine is the main product, and the reaction in question even affords a convenient method of preparing it. The diazobenzene nitrate and phenol, and the nitrosobenzene are doubtless secondary products due to the

action of nitrous acid on the nitrosophenylhydroxylamine, for a special experiment showed that the reaction between these two substances results in the formation of diazobenzene nitrate together with a little nitrosobenzene. Nitrosophenylhydroxylamine, or, rather its potassium salt, is reduced by sodium amalgam at 0° to the isodiazotate and, in part, to phenylhydrazine, but no normal diazotate is formed; nitrosoparatolyhydroxylamine behaves in precisely the same manner. Potassium permanganate oxidises the potassium salt of nitrosophenylhydroxylamine at 0° to nitrosobenzene and potassium nitrite; the same product is obtained when sodium hypochlorite is used as the oxidising agent.

Nitrosophenylhydroxylamine can be converted into the methylic ether by treating its potassium salt with methyl alcoholic, or its silver salt with ethereal, methylic iodide, as well as by treating the hydroxylamine itself with diazomethane in ethereal solution (Abstr., 1897, i, 40). In all cases, the same oxygen-ether is obtained; in this paper, it is formulated as $\text{O}:\text{NPh}:\text{N}:\text{OMe}$, whereas in the former paper equal, if not greater, prominence was given to the formula

$\text{O} < \begin{matrix} \text{NPh} \\ \text{N} \cdot \text{OMe} \end{matrix}$. This ether, in moist ethereal solution, is reduced by

aluminium amalgam at a temperature below 0° to diazobenzene methylic ether, $\text{NPh}:\text{N}:\text{OMe}$; by zinc dust in aqueous alcoholic solution containing ammonium acetate, as well as in dilute acetic acid solution, to diazonium acetate; and by sodium amalgam in aqueous alcoholic solution, to phenylhydrazine. It is hydrolysed by aqueous methyl alcoholic potash, and by aluminium chloride in benzene solution, nitrosophenylhydroxylamine being formed.

Nitrosoparabromophenylhydroxylamine, $\text{C}_6\text{H}_4\text{Br}:\text{N}(\text{NO})\cdot\text{OH}$, is obtained by adding sodium nitrite to a cooled solution of parabromophenylhydroxylamine in aqueous alcoholic hydrochloric acid; it melts at $81\text{--}82^{\circ}$; its *potassium* and *silver* salts were prepared. By treatment of the latter with methylic iodide, as well as from the hydroxylamine itself with diazomethane, the *methylic ether* was obtained; this melts at $84\cdot5\text{--}85\cdot5^{\circ}$, and is volatile with steam. In its properties, it resembles the compound containing no bromine; it does not give the Liebermann nitroso-reaction; it is so stable that it crystallises unchanged from a hot solution of potassium dichromate and sulphuric acid; it is reduced by aluminium amalgam to parabromodiazobenzene methylic ether, and by sodium amalgam to parabromophenylhydrazine, and it is hydrolysed by aqueous methyl alcoholic potash to nitrosoparabromophenylhydroxylamine.

C. F. B.

Iodine Substitution Products of some Aromatic Alcohols, Aldehydes, and Acids. By JOHANNES SEIDEL (*J. pr. chem.*, 1898, 57, 204—206).—When an alcoholic solution of saligenin is treated with iodine in the presence of mercuric oxide, a mixture of the mono- and di-iodo-derivatives is obtained, which can be separated by means of the difference in their solubilities in warm sodium hydroxide, and purified by recrystallisation from water.

Iodosaligenin forms glistening leaflets melting at 138° and the *di-iodo-derivative* needles melting at 106° .

Di-iodosalicylaldehyde, obtained in a manner similar to the above, melts at 108° ; its *phenylhydrazone* crystallises from acetic acid in yellow needles melting at 167.5° ; its *hydrazone* forms small, yellow granules, decomposing without melting at 200° ; its *oxime*, small, white needles, decomposing without melting at 210° , and its *condensation products* with aniline and paratoluidine crystallise from alcohol in orange-yellow needles, both melting at 147.5° . Iodosalicylaldehyde could not be obtained in a pure state.

Di-iodoparahydroxybenzaldehyde forms white needles melting and decomposing above 190° ; the *oxime* crystallises in small, white needles melting and decomposing at 210° ; the *phenylhydrazone*, yellow needles melting at 159° ; the *anilide*, beautiful, dark violet plates melting at 166° ; the *paratoluidide*, steel-blue leaflets melting at 190° , whilst the *paranitranilide* forms a red, crystalline powder melting and decomposing at 210° . No condensation product could be obtained with orthonitraniline.

No iodine derivatives of anisaldehyde could be obtained when using the above method, but on heating under pressure with iodine and iodic acid, *iodanisaldehyde* melting at $107-108^{\circ}$ is obtained, together with a large amount of iodanisic acid; the latter is being further investigated, as also is the action of iodine on coumarin under varying conditions. A. W. C.

The Silver Salt of 4-Nitro-2-amidobenzoic Acid and its Behaviour with Alkyl and Acidyl Haloids. By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1898, 20, 217—222).—4-Nitro-2-acetamidobenzoic acid, prepared by oxidising 4-nitro-2-acetotoluidide with 1 per cent. potassium permanganate, crystallises from alcohol in pale yellow needles, melts at about 215° , and is converted into its *sodium* salt, a bright yellow powder, by adding sodium ethoxide to its alcoholic solution; the *silver* salt is a yellow powder, which is not affected by light.

Curtius (Abstr., 1884, 1306) has prepared the ethylic and methylic salts of acetamidoacetic acid by treating the silver salt of the latter with ethylic or methylic iodide respectively. The authors find similarly that when either of the salts described above is heated with ethylic iodide in a sealed tube at 190° , *ethylic 4-nitro-2-acetamidobenzoate* is formed, which crystallises from alcohol or light petroleum in bright yellow plates or flattened prisms, and melts at 112° ; cold sodium hydroxide converts this into sodium 4-nitro-2-acetamidobenzoate, whilst alcoholic sulphuric acid removes the acetyl group only. 4-Nitro-2-amidobenzoic acid crystallises from alcohol in bright red needles, and, when heated, darkens at 260° , and melts and decomposes at 264° . The *ammonium* salt is readily soluble in water, and the same is true of the *sodium* salt although it is sparingly soluble in alcohol; the *silver* salt is a pinkish powder which darkens on being heated; the *methylic* salt, prepared by boiling the acid with methylic alcohol and sulphuric acid, crystallises from alcohol or light petroleum in dark-orange needles, and melts at 157° ; the *ethylic* salt forms dark-orange plates and is easily soluble in alcohol and benzene.

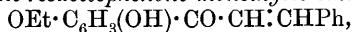
On heating silver 4-nitro-2-amidobenzoate with acetic chloride, the

acetyl derivative of the acid is alone obtained, no mixed anhydride being formed; silver anthranilate behaves similarly under the same conditions.

Silver 4-nitro-2-amidobenzoate, on being heated during three days with ethylic iodide, is converted into a mixture of 4-nitro-2-ethyl amidobenzoic acid and its ethylic salt; the former crystallises from alcohol and benzene in golden-yellow plates, and melts at 223°, whilst the latter, which is formed in smaller quantity, separates in pale yellow needles and melts at 80°. The action is therefore analogous to that of ethylic iodide on the alkali salts of the amidobenzoic acids.

W. A. D.

Synthesis of 3-Hydroxyflavone. By T. EMILEWICZ and STANISLAUS VON KOSTANECKI (*Ber.*, 1898, 31, 696—705).—2-Acetoxybenzylideneacetophenone dibromide reacts with alcoholic potash, yielding *α*-coumarylphenylketone, $C_6H_4 \begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix} \geq C \cdot CPh$, (*Abstr.*, 1896, i, 239). *Benzylidene-resacetophenone monethylic ether*,

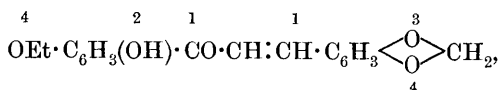


is obtained in the form of its sodium derivative when resacetophenone monethylic ether (10 grams) and benzaldehyde (5.9 grams) are dissolved in alcohol, and 50 per cent. sodium hydroxide (20 grams) is added to the warm solution, the whole being kept in a warm place for some time. The free monethylic ether is precipitated on the addition of dilute acid, and, after recrystallisation from alcohol, forms yellow needles melting at 104°; it is insoluble in cold aqueous alkalis, and is decomposed by boiling sodium hydroxide solution. Its *acetyl* derivative crystallises in yellow needles melting at 74—75°, and yields a *dibromide* crystallising in needles and melting at 118—119°. When the alcoholic solution of this dibromide is treated with potassium hydroxide, 3-ethoxyflavone, $OEt \cdot C_6H_3 \begin{smallmatrix} O-CPh \\ | \\ CO \cdot CH \end{smallmatrix}$, is formed; this crystal-

lises from alcohol, or, still better, from benzene, in needles melting at 138—139° and does not resemble Brüll and Friedländer's 3-methoxyflavone (*Abstr.*, 1897, i, 221), which is in reality 3-methoxybenzylidene coumaranone. Brüll and Friedländer's compound yields a yellow solution with sulphuric acid, whereas ethoxyflavone gives a pale blue solution with an extremely characteristic blue fluorescence. When fused with potash according to Piccard's method, ethoxyflavone yields acetophenone, resacetophenone monethylic ether, resacetophenone, resorcinol, and benzoic acid. When boiled with concentrated sodium ethoxide solution, it is decomposed quantitatively into resacetophenone monethylic ether and benzoic acid.

3-Hydroxyflavone, which is obtained when the ethoxy-derivative is boiled for several hours with hydriodic acid (1.7), is best separated from any of the unaltered compound by the aid of dilute sodium hydroxide; it crystallises from alcohol in colourless needles melting at 240°; its solutions in alkalis are of a pale yellow colour and exhibit no fluorescence, whereas its sulphuric acid solution is colourless and has a strong blue fluorescence. Its *acetyl* derivative crystallises in colourless needles melting at 129—130°.

Piperonal-resacetophenone monethylic ether,



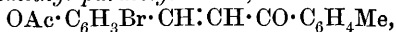
obtained from piperonal and resacetophenone monethylic ether in the presence of strong alkali, crystallises in large yellow or orange coloured plates and melts at 160° ; it is insoluble in aqueous alkalis, and on boiling with sodium hydroxide solution is decomposed. Its *acetyl* derivative crystallises in yellow needles melting at $100-101^\circ$, and yields a *dibromide* crystallising in colourless needles and melting at 130° . The dibromide, when treated with alcoholic potash, yields a compound, $\text{C}_{18}\text{H}_{14}\text{O}_5$. J. J. S.

Synthesis of Flavone Derivatives. By W. FEUERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1898, **31**, 710—719.)—*Phenacylidene-flavene*, $\text{C}_{23}\text{H}_{16}\text{O}_2$, obtained when 2-hydroxybenzylidenediacetophenone is boiled for a short time with 10 per cent. hydrochloric acid, crystallises from alcohol, in which it is fairly readily soluble, in intensely yellow needles melting at 131° ; the crystals are coloured orange by concentrated sulphuric acid, and the acid solution has a yellow colour and blue fluorescence. 2-Bromophenacylidene-flavene, $\text{C}_{23}\text{H}_{15}\text{BrO}_2$, is obtained in a similar manner from Cornelson and Kostanecki's 5-bromo-2-hydroxybenzylidenediacetophenone; it is advisable, however, to add a small quantity of alcohol to facilitate the reaction. It crystallises in reddish-yellow needles, melts at $169-170^\circ$, is turned orange coloured by sulphuric acid, in which it dissolves, giving a yellow solution with a green fluorescence. Parahomosalicylaldehyde yields two condensation products with acetophenone. When Bablich and Kostanecki's method (*Abstr.*, 1896, i, 239) is employed, 2-Hydroxy-5-methylbenzylidenediacetophenone, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH} : \text{CH} \cdot \text{COPh}$, is the chief product; it crystallises from alcohol in yellow plates, melts and decomposes at 146° , dissolves in dilute sodium hydroxide solution, and, on the addition of concentrated alkali, a yellowish-red sodium derivative crystallises out. Its *acetyl* derivative, obtained by the action of acetic anhydride and dry sodium acetate, crystallises in long, yellowish, glistening prisms.

When parahomosalicylaldehyde (1 mol.) reacts with acetophenone (2 mols.) in the presence of an excess of sodium hydroxide (*Abstr.*, 1896, i, 240), the chief product is 2-hydroxy-5-methylbenzylidenediacetophenone, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}(\text{CH}_2\text{COPh})_2$, which crystallises from alcohol in short, colourless prisms melting at 151° . When boiled with hydrochloric acid, it yields 2-methylphenacylidene-flavene, $\text{C}_{23}\text{H}_{15}\text{MeO}_2$, which crystallises in thin, glistening, yellow needles melting at $156-157^\circ$. 4':4''-Dimethylphenacylidene-flavene, $\text{C}_{23}\text{H}_{14}\text{Me}_2\text{O}_2$, obtained from 2-hydroxybenzylidenebismethyl paratolyl ketone, crystallises from alcohol in reddish-yellow needles melting at 145° .

Bromosalicylaldehyde ($\text{COH} : \text{OH} : \text{Br} = 1 : 2 : 5$) reacts with paratolyl methyl ketone, yielding 5-bromo-2-hydroxybenzylidenemethyl paratolyl ketone, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Me}$, which crystallises in yellow needles melting and decomposing at 196° , and 5-bromo-2-hydroxybenzylidenebismethyl paratolyl ketone, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}(\text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Me})_2$, crystallising in colourless plates and melting at 158° . The two compounds are readily separated by the aid of warm sodium hydroxide

solution, in which the former compound is readily soluble. 5-Bromo-2-acetoxybenzylidenemethyl paratolyl ketone,



melts at 153°. 2-Bromo-4':4'-dimethylphenacylidene-flavene crystallises in yellow needles melting at 176—177°.

These phenacylidene-flavene derivatives are stable towards aqueous potash, but are readily hydrolysed by sodium ethoxide. When phenacylidene-flavene (10 grams) was heated for several hours on the water bath with 20 grams of sodium dissolved in 200 grams of alcohol, the products isolated were acetophenone, orthohydroxyacetophenone, and benzoic acid. *Orthohydroxyacetophenone* is a colourless oil boiling at 218°; it yields a sparingly soluble yellow sodium derivative, gives a violet coloration with ferric chloride, and reacts with an alcoholic solution of benzaldehyde in the presence of sodium hydroxide, yielding 2'-hydroxybenzylideneacetophenone, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$, which crystallises in yellow needles melting at 88—89°. It dissolves slowly in cold sodium hydroxide, readily when gently warmed, and is decomposed when boiled with the alkali. 2-Bromophenacylidene-flavene, when hydrolysed in a similar manner, yields acetophenone, benzoic acid, and 5-bromorthohydroxyacetophenone; the latter crystallises from alcohol in colourless needles, melts at 61—62°, yields a sparingly soluble, crystalline sodium derivative, and reacts with benzaldehyde in the presence of 50 per cent. sodium hydroxide solution, yielding 5'-bromo-2'-hydroxybenzylideneacetophenone, which crystallises from alcohol in pale yellow needles melting at 107—108°.

The hydrolysis of phenacylidene-flavene above described agrees with

the constitution, $\begin{matrix} \text{CPh} \cdot \text{CH} \\ | \\ \text{O} - \text{C}_6\text{H}_4 \end{matrix} > \text{C} : \text{CH} \cdot \text{COPh}$, which the authors suggest.

In the formation of phenacylidene-flavene from hydroxybenzylidene-diacetophenone, acetophenone is always formed, together with another substance, which the authors have proved to be 2-hydroxybenzylacetophenone, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COPh}$; this crystallises in colourless plates melting at 91—92°, and its acetyl derivative crystallises in colourless needles and melts at 65—66°. 5-Bromo-2-hydroxybenzylacetophenone, a bye-product obtained in the preparation of 2-bromophenacylidene-flavene, melts at 94—95°, and its acetyl derivative at 67°.

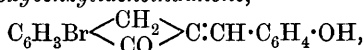
J. J. S.

Hydroxybenzylidenebromindanones. By W. KLOBSKI and STANISLAUS VON KOSTANECKI (*Ber.*, 1898, 31, 720—726).—Von Miller and Rodhe's 2-bromindanone (*Abstr.*, 1890, 1139) is best prepared by adding parabromophenylpropionic acid to sulphuric acid previously heated to 145°; the temperature, which falls slightly, is again brought to 145°, and when cold the mixture is poured into water.

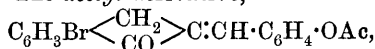
2-Bromobenzylideneindanone, $\text{C}_6\text{H}_3\text{Br} < \begin{matrix} \text{CH}_2 \\ \text{CO} \end{matrix} > \text{C} : \text{CHPh}$, is obtained when 10 per cent. aqueous sodium hydroxide is added to a warm alcoholic solution of the above compound and benzaldehyde; it crystallises in small, colourless, glistening needles melting at 162—163°, and dissolves in concentrated sulphuric acid, yielding an intense yellow solution.

The three hydroxybenzaldehydes also react with bromindanone in the presence of alkali; the yields in the cases of the ortho- and meta-compounds are good, but with the para-compound a considerable amount of a substance which is insoluble in alkali is formed. Other hydroxyaldehydes which have a hydroxy-group in the para-position, react in the same manner as parahydroxybenzaldehyde. Such aldehydes, however, react readily with bromindanone when alcoholic solutions of the aldehyde and indanone derivative are boiled with fuming hydrochloric acid.

2-Bromo-2'-hydroxybenzylideneindanone,



is obtained in the form of its sparingly soluble *sodium* derivative when a warm alcoholic solution of equivalent quantities of salicylaldehyde and bromindanone is treated with 50 per cent. sodium hydroxide (twice the weight of the aldehyde employed). The free hydroxybromobenzylideneindanone crystallises in glistening, yellow needles which carbonise at about 220°; its sulphuric acid solution has an orange colour. The *acetyl* derivative,



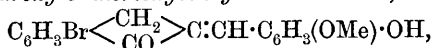
crystallises in colourless needles melting at 142°.

2-Bromo-3'-hydroxybenzylideneindanone crystallises from alcohol in long, glistening needles melting at 239°, and yields an *acetyl* derivative crystallising in colourless plates and melting at 173—174°.

2-Bromo-4'-hydroxybenzylideneindanone crystallises in minute, pale yellow needles melting at 252°; its solution in sodium hydroxide has a reddish-yellow colour, and its solution in concentrated sulphuric acid a yellow colour. Its *acetyl* derivative, which is very sparingly soluble in hot alcohol, crystallises from glacial acetic acid in colourless needles melting at 226—227°.

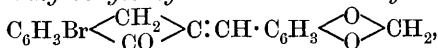
2-Bromo-3':4'-dihydroxybenzylideneindanone, obtained from protocatechuic aldehyde and bromindanone by the aid of fuming hydrochloric acid, crystallises from alcohol in brownish-yellow needles melting at 279—280°; its sodium hydroxide solution is purple, and its sulphuric acid solution yellow. It is a dye, its alumina lake having a yellow to pale orange colour, whereas the alumina lake of 4':4'-dihydroxybenzylideneindanone is red. The *diacetyl* derivative crystallises from glacial acetic acid in needles melting at 153°.

2-Bromo-4'-hydroxy-3'-methoxybenzylideneindanone,



from vanillin and bromindanone, crystallises in large, yellow needles melting at 254—255°, and yields a sparingly soluble *sodium* derivative. Its *acetyl* derivative melts at 201—202°.

2-Bromo-3'-4'-dihydroxybenzylideneindanone methylenic ether,



obtained from the action of piperonal on benzaldehyde in the presence of dilute alkali, crystallises from a mixture of acetic acid and alcohol

in glistening, straw-yellow needles melting at 223—224°; its sulphuric acid solution has a bright, cherry red colour.

These bromhydroxybenzylideneindanones differ from the simple hydroxybenzylideneindanones in their stability towards alkalis, and resemble more the hydroxybenzylidenecoumarones. All three groups of compounds resemble one another in their colour reactions; hydroxybenzylideneacetophenones also give similar colorations with sulphuric acid. All these compounds contain the double chromophore CO·C:C.

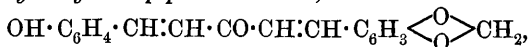
J. J. S.

2-Hydroxydibenzylideneacetone. By STANISLAUS VON KOSTANECKI and D. MARON (*Ber.*, 1898, 31, 726—730).—Haller and Kostanecki (this vol., i, 201) have already shown that compounds containing the chromophore CO·C:C·C:C are more deeply coloured than those with the simpler chromophore, CO·C:C. Experiments have been made to see whether this is also true of the complex chromophore C:C·CO·C:C, but no definite conclusions can be deduced from the results obtained.

Benzylidenepiperonalacetone, $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_5 \langle \text{O} \rangle \text{CH}_2$, obtained from piperonal and benzylideneacetone, or from benzaldehyde and piperonalacetone by Claisen and Ponder's method, melts at 115°; it dissolves in concentrated sulphuric acid, yielding a magenta-coloured solution, and, on the addition of water, a dark-coloured, flocculent precipitate is thrown down.

2-Hydroxydibenzylideneacetone, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$, is obtained when 2-hydroxybenzylideneacetone (10 grams) and benzaldehyde (6·5 grams) are dissolved in 130 grams of alcohol, the solution treated with 10 per cent. sodium hydroxide (100 grams), and at the end of 24 hours poured into dilute hydrochloric acid; it crystallises from benzene in yellow plates, and has the same melting point as 2-hydroxybenzylacetone (139°). Its alkali solutions are coloured reddish-yellow, as is also its solution in concentrated sulphuric acid; the addition of water to the latter gives a red precipitate. Its *acetyl* derivative crystallises from alcohol in pale yellow needles melting at 72—73°. The alkali solutions of 2-hydroxydibenzylideneacetone are deeper coloured than those of 2-hydroxybenzylideneacetophenone, or of 2'-hydroxybenzylideneacetophenone, probably owing to the fact that it contains the chromophore C:C in addition.

2-Hydroxybenzylidenepiperonalacetone,



crystallises from benzene in small, yellow crystals, melts at 168°, dissolves in alkalis, yielding yellowish-red solutions, and in concentrated sulphuric acid giving a reddish-purple solution; its *acetyl* derivative crystallises in amber-yellow crystals melting at 144—145°.

2-Ethoxybenzylidenepiperonalacetone crystallises from alcohol in yellow needles melting at 90°.

J. J. S.

α -Naphthaflavone. By STANISLAUS VON KOSTANECKI (*Ber.*, 1898, 31, 705—709).—*2-Benzylideneacetyl-1-naphthol*, $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$, is obtained as a red precipitate when 2-aceto-1-naphthol (10 grams),

benzaldehyde (6 grams), and warm alcohol (100 grams) are treated with 50 per cent. sodium hydroxide (20 grams) and the mixture warmed for an hour on the water bath and then poured into cold water; it crystallises from alcohol in orange-coloured plates, melts at 125—126°, and dissolves in concentrated sulphuric acid to a yellowish-red solution. Its *acetyl* derivative crystallises from dilute alcohol in yellow plates, melts at 95—96°, and yields a *dibromide* crystallising from a mixture of alcohol and benzene in colourless needles melting at 186—187°.

α-Naphthaflavone, $C_{10}H_6 \begin{smallmatrix} \text{O}-CPh \\ || \\ CO-CH \end{smallmatrix}$, is obtained when the above di-

bromide is suspended in alcohol and 30 per cent. potassium hydroxide (3 mols.) is added, the mixture well shaken, the clear solution poured into water and the precipitate thus obtained crystallised several times from alcohol. It forms pale yellow plates melting at 154—156°, and dissolves in concentrated sulphuric acid, yielding a yellow solution with a green fluorescence. When hydrolysed by boiling with concentrated sodium ethoxide, it yields 2-acetyl-1-naphthol and benzoic acid.

2-Piperonalacetyl-1-naphthol, $OH \cdot C_{10}H_6 \cdot CO \cdot CH \cdot CH \cdot C_6H_5 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} CH_2$, crystallises from a mixture of acetic acid and alcohol in pale red needles melting at 154—155°; it is insoluble in aqueous alkalis, and its sulphuric acid solution has a red colour. Its *acetyl* derivative crystallises in orange-coloured needles melting at 129—130°, and yields a *dibromide* crystallising from a mixture of chloroform and ether in yellow crusts, which decompose at 160°. *3'-4'-Dihydroxy-α-naphthaflavone methylenic ether*, $CH_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C_6H_5 \cdot C \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ CH \cdot CO \end{smallmatrix} C_{10}H_6$, obtained by the

action of potassium hydroxide on the dibromide, crystallises from its pyridine solution on the addition of alcohol in glistening, yellow needles, melting at 253—254°. It is sparingly soluble in alcohol, more readily in benzene or acetic acid; its alcoholic solution has a blue fluorescence. It dissolves in concentrated sulphuric acid, yielding a yellow solution with a feeble green fluorescence which disappears after some time. When hydrolysed with sodium ethoxide, it yields 2-acetyl-1-naphthol and piperonylic acid. J. J. S.

Ketones obtained from the Violet, and the Compounds of the Citral (Geranaldehyde) Series related to them. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1898, 31, 808—866. Compare *Abstr.*, 1895, i, 530).—This paper summarises the investigations of the fragrant oil of dried iris root which have been carried on during the past five years. The greater part of the information relating to citral, geraniol, linalool, and geranic acid has already appeared.

Pseudoionone is the product of alkaline condensation of citral with acetone (Tiemann and Krüger, *Abstr.*, 1894, i, 82). Under the influence of acids and of alkalis, it readily passes into the isomeric cyclic ketone ionone. The statement that it does not combine with hydrogen sodium sulphite is only true in the case of cold solutions, as, when boiled with the liquid, the ketone enters into combination; on liberating it from the product, it boils at 143—145° under a pressure of 12 mm.,

has the sp. gr. = 0.8984, and the refractive index $[n]_D = 1.53346$. Neither the oxime nor the phenylhydrazone is suited to the isolation of pseudoionone, difficulty being experienced in regenerating the ketone uncontaminated with ionone. The *semicarbazone* melts at 142° after recrystallisation from alcohol, benzene, and petroleum successively; it is very readily hydrolysed in alcoholic solution by an equivalent amount of sulphuric acid, yielding pseudoionone in a form which boils at $146\text{--}148^\circ$ under a pressure of 12 mm., has the sp. gr. = 0.898, and the refractive index $[n]_D = 1.5274$. The *parabromophenylhydrazone* crystallises with difficulty, and after recrystallisation from petroleum melts at $102\text{--}104^\circ$; as the corresponding derivative of ionone crystallises very readily, a convenient method of detecting pseudoionone consists in acting on it with dilute acid, and preparing the bromophenylhydrazone of the ionone thus produced. A more rapid process for the detection of pseudoionone consists in transforming the ketone into β -ionone (following abstract) by the agency of concentrated sulphuric acid, and converting the product into the semicarbazone (m. p. 148°); a third method consists in converting the ketone by means of hydriodic acid into the hydrocarbon ionene, oxidising the latter to ioniregnetricarboxylic acid, and preparing the anhydride (m. p. 214°).

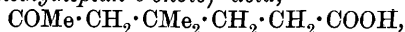
Pseudoionone is slowly oxidised by an ice cold 2 per cent. solution of potassium permanganate; on further oxidation of the filtrate with chromic acid, acetone, acetic, and levulinic acids are produced (compare Abstr., 1895, i, 646). In consideration of this behaviour, the author represents the constitution of pseudoionone by the formula $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ (compare Abstr., 1894, i, 82).

Methods of detecting ionone are described (compare Tiemann and Krüger, Abstr., 1895, i, 530), and the constitution of this substance is discussed; reasons are given in detail for ascribing to it the constitutional formula $\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ (compare Abstr., 1894, i, 83).

Hydroxyionolactone, $\begin{array}{c} \text{CH}_2\cdot\text{CMe}_2\cdot\text{CH} \\ | \\ \text{CH}_2\text{---CH} \end{array} \begin{array}{l} \text{---CO} \\ \text{---CMe}\cdot\text{OH} \\ \text{---O} \end{array}$, is prepared by

oxidising ionone with potassium permanganate; it is sparingly soluble in water, from which it crystallises, melting at 130° . The lactone is very unstable, and quickly becomes yellow when exposed to air; it gradually dissolves in caustic soda, but is reprecipitated on adding an acid. Treatment with hydrogen bromide converts it into the *bromolactone*, $\text{C}_{10}\text{H}_{15}\text{BrO}_2$, and when this is boiled with caustic alkali, it yields a dihydroxydihydrocyclogeranic acid melting at 177.5° (compare Tiemann and Semmler, Abstr., 1894, i, 85).

Geronic (4-dimethylheptan-6-onoic) acid,



which is also a product of the oxidation of ionone with potassium permanganate, is a colourless, viscous oil. The *semicarbazone* melts at 164° . Alkali hypobromite eliminates bromoform from geronic acid, giving rise to asymmetrical β -dimethyladipic acid.

In addition to hydroxyionolactone and geronic acid, asymmetrical

α -dimethylglutaric and asymmetrical dimethylsuccinic acids are produced by the oxidation of ionone. The formation of these substances is in agreement with the above expression of the constitution of ionone.

M. O. F.

Resolution of Ionone into Two Structurally Identical Forms, α -Ionone and β -Ionone. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1898, 31, 867—881. Compare Abstr., 1895, i, 530).—Ionone is the ketone obtained by Tiemann and Krüger on heating pseudoionone with dilute sulphuric acid and a small quantity of glycerol (Abstr., 1894, i, 82). Employing concentrated sulphuric acid, de Laire obtained ionone in a form which scarcely differed from ordinary ionone in physical characteristics, but which yielded different derivatives with substituted ammonias (American Patent, No. 600429, 1898). The isomeride, which has been referred to as isoionone, is structurally identical with ionone, and probably differs from it in some stereochemical respect, depending on the disposition of the $\cdot\text{CH}:\text{CH}\cdot\text{COMe}$ group in the formula

$$\begin{array}{c} \text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe} \\ | \\ \text{CH}_2\cdot\text{CH}=\text{CMe} \end{array}$$

for ionone. The two modifications of the ketone are now distinguished as α -ionone and β -ionone.

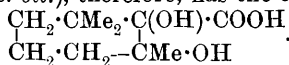
α -Ionone is prepared from commercial ionone by converting it into the oxime, crystallising this derivative from petroleum, and regenerating the ketone with dilute sulphuric acid; it boils at 123—124°, and 134—136° under pressures of 11 mm. and 17 mm. respectively. It has the sp. gr. = 0.932, and the refractive index $[n]_D = 1.4980$, whence the molecular refraction is 60.38; the value calculated for the formula $\text{C}_{13}\text{H}_{20}\text{O}$, with two ethylenic linkings, is 59.24. In certain respects the odour of α -ionone differs slightly from that of the isomeride. The oxime crystallises when the solution in low-boiling point petroleum is cooled with a freezing mixture; the derivative of β -ionone does not separate, and consequently may be removed from the isomeric substance. The oxime melts at 89—90°. The semicarbazone dissolves more readily than β -ionone semicarbazone in petroleum; it melts at 107—108° (compare Abstr., 1895, i, 530). The parabromophenylhydrazones crystallise readily from glacial acetic acid, and from methylic and ethylic alcohols; it softens at 135°, and melts at 142—143°. α -Iononeoximeacetic acid, $\text{C}_{13}\text{H}_{20}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$, is prepared from the oxime and chloracetic acid; it crystallises from petroleum, and melts at 98—99°. α -Iononehydrazone, $\text{C}_{13}\text{H}_{20}\cdot\text{N}\cdot\text{N}\cdot\text{C}_{13}\text{H}_{20}$, melts at 99°. Both α -ionone and β -ionone, when oxidised with potassium permanganate, yield the same products as ionone (preceding abstract), namely, hydroxyionolactone, geronic acid, asymmetrical β -dimethyladipic acid, and asymmetrical α -dimethylglutaric acid. Furthermore, the hydrocarbon ionene, obtained by the action of hydriodic acid on the ketone, differs in no respect from ionene prepared from β -ionone.

β -Ionone is obtained from the mixture of ketones by means of the semicarbazone, which crystallises more readily than the corresponding derivative of the α -ketone; it boils at 127—128.5°, 134.5—135.5°, and 140°, under pressures of 10 mm., 14.5 mm., and 18 mm. respectively.

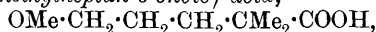
It has the sp. gr. = 0.946, and the refractive index $[n]_D = 1.521$, whence the molecular refraction is 61.70. The *oxime* is an oil, but yields the *oximeacetic acid*, which crystallises from petroleum in leaflets, and melts at 103°. The *semicarbazone* melts at 148—149°, and becomes yellow on exposure to air. The *parabromophenylhydrazone* crystallises from petroleum in large, rectangular plates, and melts at 115—116°; whilst the *hydrazone* separates from alcohol in shortened, rhombic prisms, and melts at 104—105°. M. O. F.

Constitution of Isogeranic (Cyclo-Geranic) Acid. Iso-geranionitrile. By J. C. W. FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1898, 31, 881—890. Compare Tiemann and Semmler, *Abstr.*, 1894, i, 85).—By studying the products of oxidation of isogeranic acid, the authors have shown that this compound has the constitution expressed by the formula $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{C} \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 - \text{CMe} \end{array}$; dihydroxydihydro-

isogeranic acid (*loc. cit.*), therefore, has the constitution



Isogeronic (2-dimethylheptan-6-onoic) acid,



is produced from isogeranic acid by further oxidising with chromic acid the products obtained by oxidising geranic acid with potassium permanganate; it is a viscous, colourless oil, which dissolves readily in water, alcohol, and ether. The *semicarbazone* is almost insoluble in ethylic acetate, but crystallises from alcohol in leaflets and melts at 198°. Oxidation of isogeronic acid with alkaline hypobromite eliminates one methyl group, giving rise to *unsymmetrical α-dimethyladipic acid*, which crystallises from benzene in needles, and melts at 87°; its *silver salt* is somewhat soluble in boiling water. The remaining products of oxidation of isogeranic acid are unsymmetrical α-dimethylglutaric and α-dimethylsuccinic acids.

The authors refer to the paper of Barbier and Bouveault on isogeranionitrile (*Abstr.*, 1897, i, 537). M. O. F.

A Resinous Substance from Beetroot Juice. By EDMUND O. VON LIPPMANN (*Ber.*, 1898, 31, 674—678).—The author describes an acid which he obtained in the form of a calcium salt when the juice from certain beetroots was passed over animal charcoal. In many respects it resembles Andrlik and Votoček's compound (*Zeit. Zucker-ind. Böhm.*, 20, 248). Neither the acid nor its calcium salt could be obtained in a crystalline form, and they were not analysed. When oxidised with nitric acid, it yields isophthalic acid; when fused with potash, the chief product is protocatechuic acid, and on boiling with alkali or barium hydroxide, it yields caffeic acid. J. J. S.

Ouabain. By ALBERT ARNAUD (*Compt. rend.*, 1898, 126, 346—349).—Ouabain, when crystallised from aqueous solutions, can form three different hydrates, according to the temperature at which crystallisation takes place. The hydrate, $\text{C}_{30}\text{H}_{46}\text{O}_{12} + 9\text{H}_2\text{O}$, forms between 10° and 20°, and crystallises in quadratic tables, in which according to Wyruboff, $[a:c:1:l:1:6003]$.

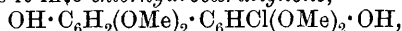
The hydrate that forms at about 30° contains $4\text{H}_2\text{O}$, and that which is formed at about 60° contains $3\text{H}_2\text{O}$. The rotatory power of ouabain in aqueous solution is $[\alpha]_D = -30.6^{\circ}$. 100 c.c. of water dissolve, at 8° , 0.66 gram of ouabain; at 14.5° , 0.93 gram, and at 30° , 1.57 grams. Cryometric observations with aqueous and acetic acid solutions confirm the molecular weight previously attributed to the compound.

When hydrolysed with dilute acids, ouabain yields rhamnose and a red resin, which is doubtless a product of the polymerisation of the second product of the hydrolysis. Each molecule of ouabain yields one molecule of rhamnose. Emulsin, diastase and other soluble ferments have no action on ouabain, but certain microbes seem to be able to split it up into rhamnose and a crystalline product.

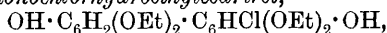
Concentrated nitric acid converts ouabain into amorphous nitro-derivatives, large quantities of oxalic acid being formed if the liquid is heated. Dilute nitric acid yields crystallisable nitro-derivatives, which seem to be acidic in character, and are probably derived from the second product of hydrolysis. Bromine yields an amorphous derivative containing nearly 63 per cent. of the halogen. Alkalis form, with ouabain, compounds which are extremely soluble and are not crystallisable. Sodium and potassium in presence of alcohol yield compounds which seem to be of the type $\text{C}_{30}\text{H}_{45}\text{MO}_{12}$, and with an excess of the metals more hydrogen is displaced. Acetic anhydride between 30° and 70° yields an acetin, $\text{C}_{30}\text{H}_{39}\text{O}_{12}\text{Ac}_7$, which crystallises in micaceous lamellæ melting at $270-275^{\circ}$. C. H. B.

Compounds from Lichens. By OSWALD HESSE (*Ber.*, 1898, 31, 663—665. Compare Abstr., 1897, i, 630).—*Rhizocarpic acid* has the formula $\text{C}_{28}\text{H}_{22}\text{O}_7$ (compare Zopf, Abstr., 1895, i, 297), and can readily be separated from parellic acid and rhizonic acid which accompany it in *Rhizocarpon geographicum f. contiguum*. *Rhizonic acid*, $\text{C}_{19}\text{H}_{20}\text{O}_7$, forms prisms which are almost cubical, and melts and decomposes at 185° ; when boiled with aqueous baryta, it yields carbonic anhydride, betorcinol and *rhizoninic acid*, $\text{C}_{10}\text{H}_{12}\text{O}_4$, which has the constitution of a *methyl-betorcinolcarboxylic acid*, $\text{OH}\cdot\text{C}_8\text{H}_7(\text{OMe})\cdot\text{COOH}$. In a previous paper (Abstr., 1897, i, 255) ethylic hæmatommate is erroneously included among the naturally occurring derivatives of betorcinol instead of methylic betorcinolcarboxylate. A. H.

The Lignone Colouring Matters and Cœrulignone. By CARL LIEBERMANN and GUSTAV CYBULSKI (*Ber.*, 1898, 31, 615—621).—When cœrulignone is treated with acids, derivatives of the colourless hydro-derivative are formed. A methyl alcoholic solution of hydrogen chloride converts it into *chlorhydrocœrulignone*,



which crystallises in small, colourless needles and melts at 141° . When ethylic alcohol is employed, the methoxyl groups are replaced by ethoxyl and *monochlorhydroethylecdrivet*,

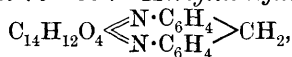


is produced which crystallises in colourless needles melting at $129-130^{\circ}$ and yields a diacetyl-derivative which crystallises in colourless needles and melts at $94-96^{\circ}$. When this compound is treated with alcoholic ferric chloride, it is not converted into the corresponding quinone, but

yields a compound which forms small, red crystals melting at 159° , and probably has the constitution $\text{OH} \cdot \text{C}_6\text{HCl}(\text{OEt})_2 \cdot \text{C}_6\text{H}_2(\text{OEt}) < \text{O} > \text{O}$.

Aqueous hydrobromic acid converts cœrulignone into a mixture of hydrocœrulignone with brominated derivatives, whilst in alcoholic solution it yields a mixture of bromo- and dibromo-hydrocœrulignone. Acetic acid yields colourless hydrocœrulignone along with a dark brown oxidation product. The lignone colouring matters behave in a similar manner, but undergo change much more readily both in the presence of reducing agents and of acids. Thus the derivative of ψ -cumidine is converted by alcoholic sulphurous anhydride into *leuco-hexamethyl-lignone blue*, $\text{C}_{32}\text{H}_{86}\text{N}_2\text{O}_4$, which crystallises in colourless needles, and is reconverted into the colouring matter by exposure to the air or by treatment with ferric chloride. Dimethyl-lignone blue (derived from paratoluidine) is converted by methylic alcoholic hydrogen chloride into *leucochlorodimethyl-lignone blue*, $\text{C}_{28}\text{H}_{27}\text{ClN}_2\text{O}_4$, which is reconverted into the colouring matter by ferric chloride. The addition of acids to these quinonic substances therefore converts them into colourless compounds, and this explains the fact that the colouring matters themselves in alcoholic solution, and their sulphonic acids in aqueous solution, readily decompose, especially in the presence of an acid, and are, on this account, valueless for dyeing.

Dinitrodimethyl-lignone blue, $\text{C}_{28}\text{H}_{24}\text{N}_4\text{O}_8$, prepared from orthonitro-paratoluidine, melts at $78-80^{\circ}$. *Methylenelignone blue*,



prepared from diparadiamidodiphenylmethane, is strongly hygroscopic.
A. H.

Phyllocyanic Acid and Phyllocyanates. By A. GUILLEMARE (*Compt. rend.*, 1898, 126, 426—428.)—In order to prepare phyllocyanic acid, green leaves are treated at 90° with about one-quarter of their weight of sodium hydroxide solution of sp. gr. = 1.056. The liquid is saturated with carbonic anhydride, the upper part of the vessel being left full of this gas, and an excess of hydrochloric acid diluted with 100 vols. of water is added gradually, care being taken to avoid rise of temperature. The precipitated phyllocyanic acid is washed and is instantly and completely soluble, without decomposition, in a 1 per cent. solution of sodium or potassium hydroxide, or even ammonia. In order to purify it, the precipitate is treated with a dilute solution of an alkali carbonate in quantity insufficient to dissolve the whole of it, and this process may be repeated several times.

The properties of the compound thus obtained are identical with those of Fremy's phyllocyanic acid. The author has prepared, and will describe later, the phyllocyanates of the alkalis, alkali-earths, iron, aluminium, zinc, cadmium, copper, strontium, lead, mercury, silver, quinine, and cinchonine.
C. H. B.

Dihydropyrroline, Pyrrolidine, Tetrahydropyridine and Piperidine Derivatives. By ANDREAS LIPP (*Ber.*, 1898, 31, 589—591.)—The author expresses surprise at the invasion of his

domain by Hielscher (this vol., i, 338) and Ladenburg (*ibid.*, 338, 339), and complains that the latter has misrepresented him in certain points. C. F. B.

Halogen Derivatives of Pyridine. By P. F. TROWBRIDGE and O. C. DIEHL (*J. Amer. Chem. Soc.*, 1897, 19, 558—575. Compare Abstr., 1896, i, 186 and 316, and this vol., i, 270).—*Pyridine hydriodide dibromide*, $C_5NH_5HI.Br_2$, formed on passing carbonic anhydride saturated with bromine through an aqueous solution of pyridine hydriodide, crystallises from alcohol in reddish-brown plates and melts at 172—175°. *Pyridine methiodide dibromide*, $C_5NH_5MeI.Br_2$, prepared similarly, crystallises from absolute alcohol in orange-yellow needles and melts at 61—62°; *pyridine ethiodide dibromide*, $C_5NH_5EtI.Br_2$, separates from alcohol in orange-yellow crystals and melts at 25—26°.

When chlorine is passed into aqueous pyridine hydriodide, a *trichloride*, $C_5NH_5HI.Cl_3$, of the latter is formed, which crystallises from alcohol and melts at 176°. *Pyridine methiodide tetrachloride*, $C_5NH_5MeI.Cl_4$, prepared similarly, is a canary-yellow powder, which melts at 185°, and is probably identical with the substance formed on passing chlorine into a mixture of pyridine methochloride iodochloride, and potash (Bally, Abstr., 1888, 964). *Pyridine ethiodide tetrachloride*, $C_5NH_5EtI.Cl_4$, melts at 123°.

The authors were unable to prepare the compound, $(C_5NH_5Br_2)_2.HBr$, obtained by Grimaux (Abstr., 1882, 1215) by acting on pyridine with bromine; on passing bromine vapours through a solution of pyridine in chloroform, *pyridine tetrabromide*, $C_5NH_5Br_4$, separated. The latter melts at 58·5°, and on standing loses bromine and is converted into a *dibromide*, $C_5NH_5Br_2$, which melts at 94—95°.

Pyridine hydrobromide forms colourless, transparent scales, and melts and decomposes at 200°. *Pyridine methobromide*, $C_5NH_5MeBr + \frac{1}{2}H_2O$, prepared by passing methylic bromide through well-cooled pyridine, separates from alcohol in large crystals, and melts and partially decomposes at 135·5°; *pyridine ethobromide* obtained by warming pyridine with ethylic bromide, separates from alcohol in white crystals, and melts at 111—112°.

Iodine dissolved in alcohol or potassium iodide solution, displaces the bromine of pyridine hydrobromide, forming the pyridine hydriodide periodides described in a former paper (this vol., i, 270). Under the same conditions, pyridine methobromide yields the pentiodide, $C_5NH_5MeI.I_4$, whilst from pyridine ethobromide an uncrystallisable product is obtained, which does not contain bromine and probably consists principally of the pentiodide, $C_5NH_5EtI.I_4$.

A *perbromide*, $(C_5NH_5HBr)_2.Br_3$, is formed when an excess of bromine is aspirated through aqueous pyridine hydrobromide; it separates from alcohol in stable, dark-orange coloured crystals, melts at 125°, and is probably identical with the compound, $(C_5NH_5Br_2)_2.HBr$, described by Grimaux (*loc. cit.*) as formed by the action of bromine on pyridine, although the latter is stated to be unstable and to melt at 126°. When less bromine is used, pyridine hydrobromide gives rise to a *monobromide*, $C_5NH_5HBr.Br$, which crystallises from alcohol and melts at 93°.

Pyridine methobromide dibromide, C_5NH_5MeBr, Br_2 , separates from alcohol in orange-red crystals, but is decomposed by acetone, and melts at 66° . *Pyridine ethobromide dibromide* is similar to the methyl compound and melts at 35° .

When chlorine is passed into aqueous pyridine hydrobromide, a somewhat unstable *substance* is formed which melts at 51° and probably has the composition $C_5NH_5, HCl, BrCl$. Pyridine methobromide, under the same conditions, yields a *dichloride*, $C_5NH_5, MeBr, Cl_2$, which is not stable, whilst from pyridine ethobromide, the *compound*, $C_5NH_5, EtBr, Cl_2$, is obtained.

On adding an excess of alcoholic iodine to pyridine hydrochloride, the chlorine is eliminated and the heptiodide,* C_5NH_5, HI, I_6 (this vol., i, 270), melting at $71-72^\circ$, is obtained; pyridine methochloride, under the same conditions, gives rise to pyridine methiodide tetriodide, whilst from pyridine ethochloride no definite compound could be prepared.

Pyridine hydrobromide dibromide, $C_5NH_5, HBr, Br_2 + 2H_2O$, formed on saturating with bromine a solution of pyridine in dilute hydrochloric acid, crystallises from alcohol in prisms and melts at $118-120^\circ$. On adding bromine to a chloroform solution of pyridine hydrochloride, the *perbromide*, C_5NH_5, HBr, Br , is formed; it crystallises in stellar aggregates of golden needles and melts at 88° . Pyridine methochloride yields with bromine a yellow *compound*, probably $C_5NH_5, MeBr, Br$, which melts at $82-83^\circ$, and a crystalline, orange-coloured *substance* melting at 55° , which is free from chlorine, and is probably the compound described by Ostermayer (Abstr., 1885, 813) as $C_5NH_5, MeBr, Br_2$, melting at 48° . When, however, pyridine methobromide is brominated, the *dibromide*, $C_5NH_5, MeBr, Br_2$, obtained melts at 66° . *Pyridine ethobromide dibromide*, $C_5NH_5, EtBr, Br_2 + 2H_2O$, formed on passing bromine vapours through aqueous pyridine ethochloride, melts at 15° .

Chlorine does not produce perchlorides with either pyridine hydrochloride, methochloride, or ethochloride.

W. A. D.

Eupphthalmine. By CARL D. HARRIES (*Ber.*, 1898, 31, 665-666. Compare Abstr., 1897, i, 552).—Phenylglycolyl-N-methyl- β -vinyl-diacetonalkamine has been found to be a powerful mydriatic, without affecting the accommodation, and has been termed *eupphthalmine*. The *hydrochloride*, $C_{17}H_{25}O_3N, HCl$, is a stable, snow-white, crystalline product, which, after recrystallisation, loses the deliquescent character possessed by the crude material precipitated by hydrogen chloride from an ethereal solution of the base. It melts at $183-184^\circ$, and is very readily soluble in water. The *salicylate*, $C_{17}H_{25}O_3N, C_6H_4(OH) \cdot COOH$, melts at $115-116^\circ$.

A. H.

γ -Halogen-derivatives of Piperidine. By HERMANN PAULY and CARL D. HARRIES (*Ber.*, 1898, 31, 666-668). γ -Iodo- and γ -bromopiperidine can be obtained by the action of the corresponding hydracids on vinyl-diacetonalkamine. γ -Iodotrimethylpiperidine, $C_8H_{16}NI$, prepared by the action of hydriodic acid on either stereoisomeric form of vinyl-diacetonalkamine, is identical with the product obtained by E. Fischer by the addition of hydrogen iodide to the corresponding acetone.

* The melting point of this compound is given as $63-64^\circ$ in the paper referred to.

γ -Bromotrimethylpiperidine, $\text{NH} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CMe}_2 - \text{CH}_2 \end{smallmatrix} \text{CHBr}$, is a crystalline mass melting at 16° ; its *hydrobromide*, $\text{C}_8\text{H}_{16}\text{NBr}$, HBr , is readily soluble in water and crystallises in pointed prisms, whilst the *picrate* forms brownish-yellow, quadratic tablets melting at 188 — 190° . The iodobase reacts with silver mandelate to form *vinylidiacetonine mandelate* melting at 147° .
A. H.

Action of Bromine on Triacetonamine. By HERMANN PAULY (*Ber.*, 1898, 31, 668—674).—When aqueous triacetonamine is treated with a solution of bromine in aqueous potassium bromide, *N*-bromotriacetonamine, $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{smallmatrix} \text{NBr}$, is obtained as a pale yellow precipitate; it crystallises in long, ribbon-like forms melting at 44° , liberates iodine from potassium iodide, and does not form salts with acids. When the filtrate from this compound, or a solution of triacetonamine hydrobromide is treated in the same way with bromine, *perbromotriacetonamine hydrobromide*, $\text{C}_9\text{H}_{17}\text{NO} \cdot \text{HBr} \cdot \text{Br}_2$, is precipitated; this crystallises in golden yellow, flat needles, which decompose at 71 — 72° , and are so unstable that the compound could not be analysed. When the perbromide is heated at 80 — 90° , hydrogen bromide is evolved and *dibromotriacetonamine hydrobromide*, $\text{C}_9\text{H}_{15}\text{NOBr}_2 \cdot \text{HBr}$, formed, the same product being also obtained when bromine is added to a strongly acid solution of triacetonamine hydrobromide at 80 — 90° ; it is sparingly soluble in most solvents, but crystallises from boiling hydrobromic acid in small, six-sided tablets, which decompose at 203° . The *free base* crystallises from benzene in slender needles, which have a satiny lustre and decompose at 140 — 150° . When either the free base or the hydrobromide is rapidly distilled with steam, an oil passes over which solidifies on standing, and then crystallises in pale emerald green prisms melting at 60 — 61° . This compound, which appears to be an isomeride of dibromotriacetonamine, dissolves in hydrobromic acid, forming a solution from which it is reprecipitated by sodium carbonate. When dibromotriacetonamine is heated with water for some time and then distilled in steam, the oil which passes over contains no bromine, boils at about 170° , and has an odour resembling that of menthol. Owing to the small quantity obtained, the further properties of this compound could not be examined. Dibromotriacetonamine reacts with silver benzoate to form *benzoyloxybromotriacetonamine*, $\text{C}_{16}\text{H}_{20}\text{NO}_3\text{Br}$, which crystallises in slender needles melting at 114° . *Imidotriacetonamine*, $\text{C}_9\text{H}_{16}\text{N}_2\text{O}$, is formed by the action of ammonia on dibromotriacetonamine-hydrobromide, and crystallises in slender prisms, melts at 180 — 181° , readily sublimes in needles, turns litmus paper blue, and is poisonous. The *hydriodide*, $\text{C}_9\text{H}_{16}\text{N}_2\text{O} \cdot \text{HI}$, crystallises in needles and the *platinichloride*, which is readily soluble in water, forms orange-coloured prisms; the *hydrochloride* and *hydrobromide* are both very readily soluble in water. The exact constitutions of dibromotriacetonamine and the imidobase have not yet been ascertained.
A. H.

Action of Phosphorus Pentachloride on 1-Alkylpyridones and 1-Alkylquinolones. By OTTO FISCHER (*Ber.*, 1898, 31, 609—612. Compare *Abstr.*, 1893, i, 282).—The alkylpyridones and

alkylquinolones are in many respects analogous to the aposafranones, but, as in the case of the last-mentioned compounds, it is doubtful whether they are ketones or anhydrides. The aposafranones, when treated with phosphorus pentachloride, yield dichlorides such as $N \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{Cl} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{NPhCl}$, in which the two chlorine atoms have different functions, and would appear from this reaction to be anhydrides of the type $O \begin{smallmatrix} \text{C}_6\text{H}_3\text{:N} \\ \text{NR} \end{smallmatrix} \text{C}_6\text{H}_4$. The following experiments were undertaken to ascertain how pyridones and quinolones behave with the same reagent, and it has been found that they lose an alkyl chloride and simply yield an α -substituted pyridine or quinoline, so that no conclusion can be drawn as to their constitution.

α -Methylpyridone (Decker, Abstr., 1892, 729 ; 1893, i, 279), when treated with phosphorus pentachloride, forms methylic chloride and α -chloropyridine, identical with that described by von Pechmann and Baltzer (Abstr., 1892, 208). N-Methylquinolone and the corresponding ethyl derivative both yield α -chloroquinoline.

This reaction affords an excellent method of preparing the α -chloro-derivatives of pyridine and quinoline, since the corresponding pyridones and quinolones are easily accessible. A. H.

Influence of Constitution on the Formation of Ring Compounds. By MAX SCHOLTZ (*Ber.*, 1898, 31, 627—632. Compare this vol., i, 305).—The law previously formulated that ortho-xylylenic bromide reacts with ortho-substituted aromatic amines to form derivatives of xylylenediamine, but with all other amines to form derivatives of dihydroisoindole, has been confirmed by the examination of a number of different aromatic amines containing various groups in various positions to the ring.

Aniline reacts with ortho-xylylenic bromide dissolved in alcohol or chloroform, to produce phenyldihydroisoindole, which melts when pure at 170—171° instead of 165° as previously stated. According to Leser (Abstr., 1884, 1313), the product consists of diphenylortho-xylylenediamine, melting at 172°, but a repetition of his experiment shows that the compound obtained by him was in reality the indole derivative.

Metabromophenyldihydroisoindole, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$, crystallises in colourless needles melting at 112°, whilst the *parabromo*-compound also forms needles and melts at 184°. *Metachlorophenyldihydroisoindole* crystallises in arborescent groups of needles melting at 101°, whilst the *parachloro*-compound crystallises in plates and melts at 170°. *Metanitrophenyldihydroisoindole* crystallises in orange-red, lustrous needles melting at 177°, whilst the *paranitro*-derivative crystallises in yellow needles. Orthonitraniline, on the other hand, yields *diortho-nitrophenylxylylenediamine*, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, which crystallises in yellow needles melting at 211—212°.

Orthamidobenzoic acid reacts like other ortho-substituted amines, and yields *xylylenebisamidobenzoic acid*, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH})_2$, which is sparingly soluble in hot water and melts at 259—260°. The *barium* and *calcium* salts are soluble in hot water. With xylylenic

bromide, metamidobenzoic acid yields *dihydroisindolebenzoic acid*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} N \cdot C_6H_4 \cdot COOH$, which crystallises in colourless needles melting at 246—247°. The *potassium*, *sodium*, and *ammonium* salts are but sparingly soluble in water. A. H.

The Base Prepared by E. Fischer from Methylketol and Methylic Iodide. By KARL BRUNNER (*Ber.*, 1898, 31, 612—615).—The base, $C_{12}H_{15}N$, obtained by Fischer and Steche (*Abstr.*, 1888, 298) by the action of methylic iodide on methylketol, has been hitherto regarded as trimethyldihydroquinoline, but it does not yield quinoline derivatives on oxidation, indolinone being produced (*Ciamician, Abstr.*, 1897, i, 101).

This base is formed when methylisopropylmethylphenylhydrazone is treated with alcoholic zinc chloride; the hydriodide, therefore, has the constitution $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{NMe}_1 \end{smallmatrix} \text{CMe}$, whilst the free base is either $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{NMe} \end{smallmatrix} \text{CMe}$ or $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{NMe} \end{smallmatrix} \text{C} \cdot \text{CH}_2$. A. H.

Heumann's Synthesis of Indigo. By W. HENTSCHEL (*J. pr. chem.*, 1898, 57, 198—201).—In repeating Heumann's process for the production of indigo, namely, fusing phenylglycine with potash, the author finds that the yield is only from 8.6—11.5 per cent. of the theoretical, and the major portion of the phenylglycine can be recovered unchanged. If the residue, after precipitating the colouring matter, is remelted with potash, a further quantity of indigo is obtained.

Attempts to improve the process have so far proved unsuccessful, but the author proposes to further investigate the matter. A. W. C.

Glauconic Acids, a New Group of Quinoline Dyes. By OSCAR G. DOEBNER (*Ber.*, 1898, 31, 686—696).—The name glauconic acids is given to a series of dyes obtained by the action of aniline or para-alkyl derivatives of aniline on pyruvic acid and formaldehyde. Their salts are bluish-violet dyes, and, like the cyanines and quinoline red, are not at all fast as regards light and acids. *Hydroglauconic acid* $CH(C_6H_3 \begin{smallmatrix} \text{NH} \text{---} \text{CHMe} \\ \text{C(COOH)} \text{:CH} \end{smallmatrix})_3$, is prepared by gradually adding pyruvic acid (100 grams) to a warm solution of aniline (50 grams) in absolute alcohol (150 grams) contained in a dish on a water bath; at the end of 15 minutes, the evolution of carbonic anhydride ceases and 40 per cent. formaldehyde (50 grams) is gradually run in; the colour then changes to brown, and carbonic anhydride is again evolved. The mixture is now heated for an hour on the water bath, fresh alcohol being added if necessary, and after remaining for 6 hours, the cold mixture is treated with a small quantity of alcohol and then a large quantity of acetone added, when the hydroglauconic acid is thrown down in the form of yellow aggregates. After being rubbed in a mortar with ether and well washed with the same solvent, it may be recrystallised from hot methylic alcohol. It melts and decomposes at about 192°, is sparingly soluble in water, acetone or ether, but dissolves more readily

in hot methylic or ethylic alcohol, is soluble in both hydrochloric and acetic acids, and is thrown down unaltered on the addition of water; it also dissolves to some extent in cold alkali, but on warming, the blue alkali salts of glauconic acid are obtained. If pyruvic acid is used in the proportion of 1 mol. instead of 2 mol. to every molecule of aniline, a sparingly soluble *anilide* of hydroglauconic acid is obtained. When subjected to dry distillation, the hydro-acid is mainly converted into carbonic anhydride and *dihydroquinaldine*, which boils at $245-247^{\circ}$; this compound can, however, be more readily obtained by heating quinaldine hydrochloride with zinc dust; it yields a *picrate* melting at 187° and a *platinochloride* crystallising in red needles.

Hydroglauconic acid can readily be oxidised to *glauconic acid* either by warming with alkalis alone, or in the presence of air, or by the aid of bromine water or of formaldehyde.

The method recommended is to heat the hydro-acid (10 grams) with alcohol (10 grams) in a dish, then to add 10 per cent. sodium hydroxide (100 c.c.), and when the mixture begins to boil to add 40 per cent. formaldehyde (15 c.c.), and to continue the boiling for a minute. On the addition of an excess of alcohol, *sodium glauconate*, $C_{34}H_{28}N_3O_6Na$, separates in the form of blue needles. The acid itself, $\begin{array}{c} \text{CH} \cdot \text{CHMe} \cdot \text{N} \\ | \\ \text{C}(\text{COOH}) - \text{C}_6\text{H}_3 \end{array} > \text{C} \left(\text{C}_6\text{H}_3 < \begin{array}{c} \text{NH} - \text{CHMe} \\ | \\ \text{C}(\text{COOH}) : \text{CH} \end{array} \right)_2$, crystallises in dark blue needles, is insoluble in water, alcohol, or ether, but dissolves in glacial acetic acid, yielding a blue solution; this blue colour changes to pink and finally disappears on the addition of zinc dust. When subjected to dry distillation, it yields dihydroquinaldine. The *sodium* salt is sparingly soluble in cold water, but dissolves in hot water, yielding a bluish-purple solution; the *calcium*, *barium*, and *aluminium* salts are obtained in the form of blue precipitates. *Hydroparethoxyglauconic acid*, obtained from paraphenetidine, pyruvic acid, and formaldehyde, is a yellow powder melting and decomposing at about 190° ; it is insoluble in water, but dissolves in alcohol or acetone. *Parethoxyglauconic acid*, $C_{40}H_{41}N_3O_9$, crystallises in dark blue needles, insoluble in alcohol but soluble in acetic acid. Its *sodium* salt, $C_{40}H_{40}N_3O_9Na$, crystallises from hot water in glistening plates, and yields a blue solution with a red fluorescence.

Hydro- β -naphthaglauconic acid, $C_{46}H_{37}N_3O_6 + 5H_2O$, obtained from β -naphthylamine, pyruvic acid, and formaldehyde, crystallises from hot methylic alcohol in large, colourless, prismatic crystals. It loses its water at 110° , and decomposes at 231° into carbonic anhydride and dihydronaphthaquinaldine. The acid is insoluble in ether, acetone or water, but dissolves in hot methylic or ethylic alcohol as well as in

dilute alkalis. *Dihydronaphthaquinaldine*, $C_{10}H_6 < \begin{array}{c} \text{NH} \cdot \text{CHMe} \\ | \\ \text{CH} : \text{CH} \end{array}$, is a

thick, yellow oil distilling somewhere above 300° ; it yields a sparingly soluble *picrate* and *platinochloride*. The yield of *β -naphthaglauconic acid*, $C_{46}H_{35}N_3O_6 + \frac{1}{2}H_2O$, obtained from the hydro-acid, is very poor (about 15 per cent.). It is deposited in the form of blue, curved needles when its alkali salts are dissolved in concentrated hydrochloric acid and then poured into water; it is insoluble in water,

alcohol, or ether, but dissolves in acetic acid, giving a blue solution. Its *sodium* salt, $C_{46}H_{34}N_3O_6Na + 8H_2O$, and *potassium* salt with $8H_2O$, are soluble in hot water, and give pure blue solutions. J. J. S.

Oxidation of Hydrazoximes. By GIACOMO PONZIO (*J. pr. chem.*, 1898, 57, 160—172).—*Phenyl-2 : 3-Dimethyl-1 : 2-oxy-pyrro-1 : 4-diazole* is obtained by the action of nitric peroxide or mercuric oxide on diacetylhydrazoxime, when oxidation takes place with elimination of two hydrogen atoms, this reaction appearing to be a general one for all hydrazoximes. It crystallises from light petroleum in prisms, often several centimetres long, melting at $92-93^\circ$, and cannot be distilled at ordinary atmospheric pressure without decomposition. A determination of the molecular weight by Beckmann's method gave 185.1 (calculated 189). It is a very feeble monacid base, forming a *hydrochloride* melting and decomposing at 120° . It does not react with phenylhydrazine, acetic anhydride, or methylic iodide, but when treated with hydriodic acid or nascent hydrogen is reduced to phenyldimethylsotriazole, for which reason, and also its behaviour towards halogen acids, the author ascribes to it the following formula, $O < \begin{array}{c} CMe - CMe \\ | \quad | \\ N \cdot NPh \cdot N \end{array}$.

Nitrophenyldimethylsotriazole, $C_2N_3Me_2 \cdot C_6H_4 \cdot NO_2$, obtained by the action of nitric acid on phenyldimethylsotriazole, crystallises from alcohol in yellow needles melting at 227° and is almost insoluble in the ordinary organic solvents. When suspended in alcohol and reduced with zinc and hydrochloric acid, the corresponding *amido*-derivative is produced, forming small, faintly-coloured prisms melting at $123-124^\circ$; its *hydrochloride* is a white, insoluble substance decomposing at 240° , and the *acetyl* derivative forms beautiful needles melting at 139° .

When phenyldimethylsotriazole is treated with bromine water, a *bromo*-derivative, $C_{10}H_{10}N_3BrO$, is obtained, which crystallises from alcohol in beautiful yellow needles melting at $109-110^\circ$. It is reduced in alcoholic solution to *bromophenyldimethylsotriazole*, $C_{10}H_{10}N_3Br$, which is also produced by the action of bromine water on the triazole; this crystallises in white needles and melts at $152-153^\circ$. *Phenyldimethylsotriazolecarboxylic acid*, $C_2N_3OMePh \cdot COOH$, obtained by the action of potassium permanganate on the free base, crystallises from light petroleum in very slender, white needles melting at 93° ; it is only slightly soluble in water, but readily in ether, chloroform, and acetone.

When phenyldimethylsotriazole is heated in sealed tubes with hydrochloric acid for 3 hours at 150° , there is produced, besides phenyldimethylsotriazole, a *chloro*-compound, $C_2N_3HMe_2PhCl$, crystallising from ether in white prisms melting at 152° and boiling at 285° ; it has no basic properties, and does not react with acetic or benzoic chlorides, acetic anhydride, or nitrous acid, but with nitric acid it yields a *mononitro*-derivative crystallising in long, glistening, yellow needles melting at 116° . On further heating with nitric acid in sealed tubes, it loses the elements of hydrogen chloride, forming mononitrophenyldimethylsotriazole, and when oxidised with chromic acid it yields a *carboxylic acid*, $C_2N_3HMePhCl \cdot COOH$, crystallising in colourless prisms and melting and decomposing at $240-242^\circ$.

The corresponding *bromo*-compound, $C_2N_3HMe_2PhBr$, forms colourless prisms melting at $150-151^\circ$, and the *iodo*-compound colourless prisms melting at 142° .
A. W. C.

Isocreatinine, a Compound obtained from the Flesh of the Haddock. By JÖRGEN E. THESEN (*Zeit. physiol. Chem.*, 1897, 24, 1—17).—On digesting the muscular tissue of the haddock (*Gadus Morrhua*) twice with a large quantity of water at 40° , and subsequently evaporating the extract, the albumin coagulates and is removed, whilst the inorganic salts are precipitated by adding alcohol; the filtrate from these is then evaporated to a thick syrup, which is repeatedly boiled with alcohol. The solution obtained deposits yellow, microscopic needles of *isocreatinine*, which, on recrystallisation from 50 per cent. alcohol, separates in beautiful, lustrous leaflets which, when heated to $230-240^\circ$, decompose without melting. Its analysis, and a determination of the molecular weight by the cryoscopic method, point to the formula $C_4H_7N_3O$; the base is thus isomeric with creatinine. The *hydrochloride*, $C_4H_7N_3O \cdot HCl$, crystallises from alcohol in dull-yellow needles, whilst the *sulphate* separates from water on adding alcohol and ether in brittle, transparent, yellow plates; the *oxalate*, $C_4H_7N_3O \cdot C_2H_2O_4$, crystallises from alcohol in long, slender, light-golden needles. Isocreatinine unites with cadmium chloride to form the *double salt*, $C_4H_7N_3O \cdot CdCl_2$, which separates from water in slender needles; the *zinc double salt*, $C_4H_7N_3O \cdot ZnCl_2$, crystallises from water on the addition of alcohol, whilst the *platinochloride*,
 $C_4H_7N_3O \cdot H_2PtCl_6 + 2H_2O$,

crystallises from dilute alcohol in red needles which lose their water at 110° and become yellow.

An alkaline solution of copper sulphate produces a blue coloration with isocreatinine, and on heating to 80° , a precipitate of cuprous and cupric oxides is formed; in presence of a reducing agent, copper sulphate produces a bright green precipitate which becomes brownish-black on heating. Isocreatinine is not precipitated by potassium mercuric iodide, potassium cadmium iodide, silver nitrate, lead acetate, copper acetate, or tannic or picric acid; and does not give the murexide or biuret reactions. Like creatinine, however, it produces a red coloration with a solution of picric acid to which a few drops of caustic soda have been added (Jaffé's reaction); and with sodium nitroprusside and caustic soda, a red coloration is produced (Weyl's reaction), which changes to blue on adding acetic acid and warming (Salkowski's reaction).

When left in contact with milk of lime, isocreatinine appears to be converted into creatine; on oxidation with 0.5 per cent. potassium permanganate, potassium oxalate is formed, but no methylguanidine. On being heated with barium hydroxide, ammonia is evolved, but no definite product could be isolated. When isocreatinine is heated for several hours with concentrated sulphuric acid containing 10 per cent. of phosphoric anhydride, no decomposition takes place, the sulphate alone being formed.

Isocreatinine differs from ordinary creatinine and from the modifications "natural" and "tabular" creatinine present in urine (Johnson,

Abstr., 1889, 165), in colour, in cupric-reducing power, and in its solubility, and that of its platinochloride and picrate, in alcohol and water; isocreatinine yields, with potassium permanganate, ammonia, but no methylguanidine, whilst creatinine gives rise to the latter, but no ammonia.

W. A. D.

Hydrocinchonine. By OSWALD HESSE (*Annalen*, 1898, 300, 42–59).—Hydrocinchonine, $C_{19}H_{24}N_2O$, was first obtained by Caventou and Willm on oxidising commercial cinchonine sulphate with potassium permanganate, the substance being an impurity of the crude alkaloid; Skraup has referred to this substance as cinchotine, but the author prefers to use the name employed by its discoverers. The proportion of hydrocinchonine occurring in cinchona bark is small, the most profitable source of the base being the bark of *Remijia Purdieana*, in which it is also found associated with cinchotine; the hydro-base is separated by means of its platinochloride.

Hydrocinchonine melts at 268–269°. A 0.6 per cent. solution in absolute alcohol has the specific rotatory power $[\alpha]_D = 204.5^\circ$, whilst a 5 per cent. solution in a mixture of chloroform and absolute alcohol (2:1) has the specific rotatory power $[\alpha]_D = 188.2^\circ$; an aqueous 5 per cent. solution of the sulphate has the specific rotatory power $[\alpha]_D = 224.2^\circ$. The normal platinochloride, $(C_{19}H_{24}N_2O)_2 \cdot H_2PtCl_6$, forms a yellow, flocculent precipitate, which soon changes into orange needles; it is anhydrous, and dissolves with difficulty in water. The acid platinochloride, $C_{19}H_{24}N_2O \cdot H_2PtCl_6$, is obtained as a yellow, flocculent precipitate, which undergoes no change in contact with the mother liquor; it contains $2H_2O$, and when prepared in an acid solution, separates in long prisms containing $4H_2O$.

The sulphate occurs in four modifications, differing from one another in the amount of water of crystallisation which they contain. The form which has been already described contains $12H_2O$, and crystallises in long, lustrous needles; a second modification crystallises in leaflets which gradually change into tetragonal double pyramids and contain $9H_2O$. The sulphate also crystallises in forms containing $6H_2O$ and $2H_2O$. A 5 per cent. solution of the dried salt in chloroform has the specific rotatory power $[\alpha]_D = 138.0^\circ$, a solution of the same concentration in absolute alcohol giving $[\alpha]_D = 160.8^\circ$.

Acetylhydrocinchonine is amorphous, and is precipitated from solutions in dilute acids by ammonia; the alcoholic solution is strongly alkaline. A 3 per cent. solution in absolute alcohol has the specific rotatory power $[\alpha]_D = 105.7^\circ$. The hydrochloride crystallises in colourless needles, and dissolves very readily in water. The platinochloride separates as a yellow, flocculent precipitate containing $1H_2O$; when gently heated with dilute hydrochloric acid, this form changes into small, orange-red needles containing $2H_2O$.

Hydrocinchoninesulphonic acid, $C_{19}H_{23}N_2O \cdot SO_3H$, is prepared by dissolving the dehydrated sulphate in concentrated sulphuric acid (sp. gr. = 1.84), and after an interval of 24 hours, pouring the liquid into cold water (compare Skraup, this vol., i, 51); it crystallises from hot water and from 50 per cent. alcohol in colourless needles containing $1H_2O$. The sulphonic acid dissolves in 714 parts of water at

15°, the solution having an acid reaction; the substance becomes anhydrous at 110°, and melts at 224°. The *hydrochloride* crystallises in colourless, lustrous needles, and contains 5H₂O; the *platinochloride* forms short, orange prisms containing 6H₂O. The *sulphate* separates in white, lustrous needles with 8H₂O; an aqueous 3 per cent. solution of the hydrated salt has the specific rotatory power $[\alpha]_D = 166^\circ$. Hydrocinchoninesulphonic acid undergoes partial hydrolysis when heated with ammonia.

M. O. F.

Pilocarpidine. By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1898, 19, 56—59).—When pilocarpine hydrochloride is fused, it is converted without loss in weight into pilocarpidine hydrochloride which is shown by the authors to contain a methyl group attached to nitrogen, whereas Merck's pilocarpidine does not. Moreover, the aurochloride of the latter melts at 120—124°, and that of the pilocarpidine obtained by fusing pilocarpine hydrochloride at 153—156°. It is therefore to be concluded that several so-called pilocarpidines exist.

A. W. C.

Action of Reducing Agents on Cholic Acid. By MICHAEL SENKOWSKI (*Monatsh.*, 1898, 19, 1—4).—In earlier researches on the reduction of cholic acid, deoxycholic acid was obtained by Mylius by the putrefaction of bile or salts of cholic acid, and by Vahlen by the action of zinc dust in acetic acid solution on cholic acid (*Abstr.*, 1897, i, 647); the author has now attempted to throw light on the constitution of cholic acid by subjecting it to the action of more energetic reducing agents.

When cholic acid is treated with hydriodic acid in presence of amorphous phosphorus, there is obtained a yellowish, brittle, resinous mass which is apparently *cholylic anhydride*, (C₂₄H₃₉O)₂O. It melts at 75—80°, but could not be obtained crystalline. Dilute potash dissolves it, forming an opalescent alkaline solution, from which concentrated potash precipitates the *potassium* salt of cholylic acid, characterised, as are also the *barium*, *lead*, *copper*, *silver*, *zinc* and *calcium* salts by not possessing a bitter taste. Cholylic acid seems not to be obtainable in the free state.

When the anhydride is dissolved in alcohol and the solution saturated with hydrogen chloride, a sticky, reddish-brown mass is produced probably consisting for the most part of *ethylic cholylate*, but neither this substance nor the *nitrile*, obtained by the action of lead thiocyanate on the anhydride, could be procured in a state fit for analysis. *Bromo-* and *nitro-*substitution products of the anhydride have been obtained, and will be dealt with more fully in a future communication.

A. W. C.

Urobilin. By F. GOWLAND HOPKINS and ARCHIBALD E. GARROD (*J. Physiol.*, 1898, 22, 451—464. Compare *Abstr.*, 1896, i, 712).—Maly's hydrobilirubin is not the same substance as urobilin, but by allowing the action of sodium amalgam on bilirubin to proceed beyond the stage indicated by Maly, a product is obtained which resembles natural urobilin very closely in its spectroscopic appearance; the E band, however, was never obtained.

In elementary composition, urinary and faecal urobilin are identical

(C, 63·58; H, 7·84; N, 4·11 per cent.). The percentage of nitrogen in hydrobilirubin is 9·57 (Maly gives 9·22). W. D. H.

Egg-albumin. By KARL DIETERICH (*Chem. Centr.*, 1897, ii, 422—423; from *Pharm. Centr.-H.*, 38, 449—453).—Fresh white of egg loses 87—88 per cent. of its weight when dried at 100° and for the preparation of a kilogram of "*albumen ovi siccum*" containing about 16—17 per cent. of water, 7—8 kilograms of the white of egg are necessary. Fresh white of egg also contains some yolk and about 1 per cent of fibrin, &c.; the latter can be removed by beating and filtering through cloth. The iodine absorption number of fresh white of egg is about 155 and that of fibrin 174—178. White of egg which contains fibrin partly dissolves in water, although with difficulty, forming a turbid solution and the residual insoluble portion (6·32 per cent. in one case) is greater than that obtained from white of egg free from fibrin (3·97 per cent.); the soluble portion of the latter, moreover, dissolves more quickly and forms a clear solution. White of egg which contains no fibrin is easily soluble in dilute (30 per cent.) acetic acid, giving a solution which remains clear on adding water or alcohol. Fibrin is insoluble in acetic acid, and hence white of egg which contains fibrin, only partially dissolves and when water or alcohol is added to the solution only the very small quantity of dissolved fibrin is precipitated. *Albumen ovi siccum* forms a transparent, horny mass, or a yellowish, tasteless, odourless powder, is insoluble in alcohol, and gives a neutral, turbid solution in water. When 5 c.c. of the aqueous solution (1/1000) is carefully warmed with 10 drops of nitric acid, there is an abundant separation of coagulated albumin. The amount of iodine absorbed by this substance should be at least 12 per cent., and the content of water 16—17 per cent. (dried at 100°). The portion insoluble in water should not amount to more than 4—5 per cent. 0·1 gram of the powder when boiled with 10 c.c. of 30 per cent. acetic acid should dissolve completely in 5 minutes, and the solution should not give a precipitate on adding 20 c.c. of water or alcohol. E. W. W.

Iodalbumin. By FRANZ HOFMEISTER (*Zeit. physiol. Chem.*, 1897, 24, 159—172).—When purified crystallised egg-albumin (20 grams) is heated during 4 hours with a mixture of potassium iodide (10 grams), potassium iodate (5 grams) and concentrated sulphuric acid (4 c.c.) dissolved in 400 c.c. of water, *iodalbumin* is precipitated as a light-brown powder which is insoluble in water; it dissolves in alkalis, but separates as a white, gelatinous precipitate on adding dilute acids, although soluble in excess. Iodalbumin, after being carefully purified by successive precipitations, contains 8·95 per cent. of iodine, none of which is removed by continued washing with water or aqueous potassium iodide. It resembles albumin in being precipitated by potassium ferrocyanide, and in giving the xanthoprotein and biuret reactions, and the sugar reaction in presence of α -naphthol (Molisch); it fails, however, to give Millon's or Adamkiewicz's reactions, and does not produce lead sulphide when boiled with alkaline lead oxide. From the latter fact, the author concludes that the sulphur exists in an oxidised (sulphonic) form in iodalbumin, and partially in the form of a mercaptan or sulphide in ordinary albumin.

On the ground of previous analyses, the author attributes to crystallised egg-albumin the composition $C_{239}H_{386}N_{58}S_2O_{73}$, whilst to iodalbumin, the formula $C_{227}H_{370}I_4N_{58}S_2O_{75}$ is given. Its formation is explained by assuming that 4 atoms of hydrogen in albumin are displaced by iodine, whilst 3 atoms of oxygen are added in the oxidation of 1 atom of sulphur; 2 mols. of a carbohydrate, $C_6H_{12}O_6$, are eliminated from, and 6 mols. H_2O added to, the molecule of albumin. This view is supported by the fact that a considerable proportion of a carbohydrate yielding a crystalline osazone was formed in the preparation of iodalbumin, owing to the hydrolytic action of the sulphuric acid employed.

When iodalbumin is digested with pepsin, peptone is formed and iodine liberated; when administered to rabbits, alkaline iodides are found in the urine after a few hours, but no toxic effects are produced.

W. A. D.

[NOTE BY ABTRACTOR.—A product, probably identical with iodalbumin and possessing all the properties of the latter, was prepared by Hopkins (this vol., i, 54 and 99) from a solution of egg-albumin; it contained, however, only 6.28 per cent. of iodine.]

Proteids of the Maize Kernel. By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1897, 19, 525—532. Compare Chittenden and Osborne, *Abstr.*, 1892, 379, 746 and 749).—By precipitating an aqueous extract of maize meal with ammonium sulphate and dissolving the precipitate in water, a solution is obtained from which the globulins can be completely removed by dialysing and subsequently heating to 80° ; if alcohol is then added, a small quantity of a *proteid* is precipitated which shows many of the reactions of the proteoses. It appears that whilst no true albumin is present in maize, three globulins can be separated; the first of these, *maysin*, formerly called “maize myosin,” is completely extracted from the meal by water alone; its solution in 10 per cent. brine coagulates at 70° , whilst that of *maize globulin*, the “albumin” of the previous paper, coagulates at 62° . *Maize edestin* is much less soluble in saline solutions than either of the foregoing; its solution in 10 per cent. brine is only partially coagulated by boiling.

Zein, extracted from maize meal by hot 85—95 per cent. alcohol, is insoluble in water and in absolute alcohol, but is easily soluble in glycerol heated to 150° , and remains unchanged when the latter solution is heated to 200° ; it dissolves without change in warm phenol and in boiling glacial acetic acid, but is insoluble in 0.5 per cent. sodium carbonate, and in 0.2 per cent. hydrochloric acid; in 0.1—2.0 per cent. caustic potash it dissolves easily, but is not converted into alkali albumin, even after heating at 40° during 24 hours. Alcoholic solutions of zein are not precipitated by tannin, picric acid, trichloroacetic acid, lead acetate, silver nitrate, mercuric chloride, ferric chloride, or potassio-mercuric iodide. The clear films produced by evaporating on glass an alcoholic solution of zein to which silver nitrate has been added, gradually turn deep red on exposure to sunlight.

In addition to the proteids described, a 0.2 per cent. solution of potash dissolves a substance which is insoluble in salt solutions and alcohol, and contains 2.38 per cent. of ash.

The following table gives analyses of the proteids present in maize meal, as well as the proportions in which they occur.

Proteid.	Percentage of maize.	Composition.				
		C.	H.	N.	S.	O.
Protease	0·06	—	—	17·00	—	—
Maysin	0·25	52·68	7·02	16·76	1·30	22·24
Maize globulin	0·04	52·38	6·82	15·25	1·26	24·29
Maize edestin.....	0·10	51·43	6·86	18·06	0·86	22·79
Zein.....	5·00	55·23	7·26	16·13	0·60	20·78
Proteid soluble in 0·2 per cent. potash.....	3·15	51·26	6·72	15·82	0·90	25·30

W. A. D.

Decomposition of Casein by Hydrochloric Acid. By THEODOR PANZER (*Zeit. physiol. Chem.*, 1897, 24, 138—141).—Purified casein was heated during 5 hours with concentrated hydrochloric acid (sp. gr. = 1·19), and during several days with its 20 per cent. solution; large quantities of glutamic acid, which was characterised by analysis and crystallographic measurement, were obtained; the statement of Cohn (*Abstr.*, 1896, i, 658) that the latter is only formed in small quantity under the above conditions is, therefore, incorrect.

W. A. D.

Organic Chemistry.

Chemical Effects of the Silent Electric Discharge. By MARCELLIN E. BERTHELOT (*Compt. rend.*, 1898, 126, 561—567, 567—575, 609—616, 616—627).—The author has made a new series of experiments on the chemical effects of the silent electrical discharge, with particular reference to the combination of nitrogen with various carbon compounds. The compound or mixture under examination was enclosed in a narrow space (about 1 mm. across), through which passed the discharge from a coil fitted with a Marcel-Deprez contact-breaker, and connected with a Leyden jar. The spark from the coil under these conditions was 12 to 15 mm. in length; the discharges were alternating. As a rule, the discharge was allowed to act for 24 hours. Liquids with a high vapour tension behaved very much like gases, whereas in the case of liquids such as oil, with a very low vapour tension, it was almost impossible to reach the limit of the reaction. In many cases, the intermediate products were examined, and were usually found to differ materially from the final products. The relative velocities of the primary and secondary reactions play an important part in determining the final result. The velocity and nature of the reactions seem to be functions of the intensity of the discharge. Under all circumstances, it is important to avoid any actual sparking. As a rule, the final equilibrium is dependent on the formation of solid or resinous products which have a low vapour tension and a low electric conductivity.

When absorption of nitrogen takes place, the product is of the nature of an amine or an amido-derivative, and frequently seems to be a poly-amine; azo-, nitroso-, and nitro-derivatives, hydrazines, hydrogen cyanide, or ammonium cyanide are not formed.

Several hydrocarbons were examined, both alone and when mixed with an equal volume of nitrogen. Methane loses about half its hydrogen, and yields a solid product, $C_{10}H_{18}$; a small quantity of acetylene is formed in the early stages of the decomposition, but afterwards disappears. In presence of nitrogen, the methane loses about half its hydrogen, and the nitrogen absorbed is rather less than one-fourth of the volume of hydrogen liberated; the solid product, which has the empirical composition C_2H_3N , and is probably a tetramine of the nature of a polymerised acetylenamine, is alkaline to litmus.

Ethane loses about one-third of its hydrogen, and the condensation product, $C_{10}H_{18}$, has practically the same composition as the product from methane, but is not identical with it. In presence of nitrogen, the solid product, $C_{16}H_{32}N_4$, is similar to that obtained from methane, except that the ratio of carbon to nitrogen in the product from ethane is twice as high as in the product from methane. Ethylene is rapidly condensed to a liquid under the influence of the discharge, whilst small quantities of acetylene and ethane are formed; the latter eventually disappear, and the solid product has the composition C_8H_{14} . In presence of nitrogen, the product is an alkaline solid of

the composition $C_{16}H_{32}N_4$, the volume of nitrogen absorbed being practically equal to the volume of hydrogen liberated.

Acetylene yields first a liquid, and afterwards a solid, which decomposes explosively when heated, and is rapidly oxidised when exposed to air. In presence of nitrogen, the phenomena are at first the same as with acetylene alone, but after a time the nitrogen is absorbed, with formation of a solid product, $C_{16}H_{16}N_2$. No hydrogen is liberated.

Propylene at first condenses rapidly to a liquid, and afterwards a solid is formed of the composition $C_{15}H_{26}$, some hydrogen being liberated. With nitrogen, the phenomena are similar, but gradually nitrogen is absorbed and hydrogen is liberated, the product, $C_{15}H_{28}N_4$, being a whitish resin with an alkaline reaction, the volume of nitrogen absorbed being practically double that of the hydrogen liberated.

Trimethylene, when alone, behaves in the same way as propylene, and yields practically the same product; but in presence of nitrogen, the product, although similar to that from propylene, contains less hydrogen, the volume of hydrogen liberated being practically equal to the volume of nitrogen absorbed.

Allylene rapidly condenses to a solid with a pungent empyreumatic odour, a small quantity of hydrogen being liberated in presence of nitrogen. No hydrogen is liberated, but the nitrogen is absorbed, and the product has the composition $C_{15}H_{20}N_2$.

Carbonic oxide is converted by the discharge into carbonic anhydride and the suboxide, C_4O_3 , as the author and Brodie showed many years ago; the suboxide is a brown solid which dissolves in water, and forms an acid solution. In presence of nitrogen, the results are the same as with carbonic oxide alone. In presence of excess of hydrogen, the two gases condense in practically equal volumes, without formation of either carbonic anhydride or acetylene. The product $(CH_2O)_n$ is a mixture of polymerides of formaldehyde, some being soluble and others insoluble in water; they have no reducing action on Fehling's solution. When the carbonic oxide is in excess and not the hydrogen, the product has the empirical composition $C_3H_4O_3$, and its aqueous solution has some reducing power. With carbonic oxide, nitrogen, and hydrogen, the product $(CH_3NO)_n$ may be regarded as a condensed formamide. When the hydrogen in the gaseous mixture is not in excess, the product is a mixture of substances which dissolve in water and yield ammonia when boiled with an alkali, and substances which are insoluble in water and seem to be related to the quinolines. The complex nitrogen derivatives may be regarded as formed by the substitution of nitrogen in the carbohydrate formed by the action of the discharge on the carbonic oxide and nitrogen.

Carbonic anhydride alone yields percarbonic anhydride and the suboxide previously described. With a mixture of carbonic anhydride with twice its volume of hydrogen, the product is a carbohydrate identical with that formed by carbonic oxide under similar conditions. If the anhydride is mixed with an equal volume of nitrogen and three times its volume of hydrogen, the residual gas contains no carbon, but consists of equal volumes of nitrogen and hydrogen; the solid product, when heated with water, yields an effervescing solution containing ammonium nitrite. It may be regarded as a mixture of ammonium

nitrite with the amido-compound formed by carbonic oxide; possibly it may be a true azo-compound dissociable by water. With 4 vols. of hydrogen instead of 6, more of the nitrogen is left.

The action of the silent discharge on carbonic oxide or carbonic anhydride in presence of hydrogen and nitrogen may be compared with the interactions of water and carbonic anhydride in plants, or with the action of heat on salts of formic acid. The general results confirm the author's earlier views as to the great importance of the CH_2O group and its reactions.

In the experiments with alcohols, the reaction was, as a rule, carried to its limit wherever possible.

With methylic alcohol and nitrogen, the latter is absorbed and an equal volume of hydrogen is liberated, together with a small quantity of carbonic oxide; the solid product contains $\text{C}_4\text{H}_{12}\text{N}_2\text{O}_4$, and is probably one of the complex amidines or their hydrates. At the beginning of the reaction, some hydrogen, methane, carbonic oxide, and carbonic anhydride are formed, and at a later stage the proportion of methane is still higher, but eventually it disappears, together with the carbonic anhydride.

Ethylic alcohol in presence of nitrogen yields hydrogen, traces of carbonic anhydride, and a solid product, $\text{C}_{10}\text{H}_{20}\text{N}_4\text{O}_5$; the hydrogen liberated per molecule of ethylic alcohol is double that liberated per molecule of methylic alcohol, and the same ratio holds good for the quantity of nitrogen absorbed. In the early stages of the reaction, ethane and carbonic oxide are formed, but subsequently disappear.

Propylic and isopropylic alcohols behave in much the same way as ethylic alcohol. Nitrogen is absorbed, and twice as much hydrogen is liberated; the solid product is $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2$.

Allylic alcohol yields a strongly alkaline solid product, the empirical formula of which is $\text{C}_9\text{H}_{16}\text{N}_2\text{O}_3$. The quantity of hydrogen liberated is very small, and is equal to about one-third of the volume of nitrogen absorbed.

Phenol, under similar conditions, absorbs nitrogen, but no other gas is liberated, and the solid remains neutral. In the case of dihydric phenols, very little nitrogen is absorbed by the meta- and para-derivatives, but the ortho-derivative absorbs a considerable quantity, and yields a neutral product. Pyrogallol absorbs a small quantity of nitrogen, and gives off small quantities of hydrogen and carbonic oxide.

Glycollic ether, with an equal volume of nitrogen, yields small quantities of ethane and hydrogen, but no carbon oxides. A volume of nitrogen equal to the volume of the glycollic ether is absorbed, and the solid product contains $(\text{C}_2\text{H}_4\text{N}_2\text{O})_n$. It is an isomeride of cyanamide hydrate.

Methylic ether, with excess of nitrogen, yields the substance $\text{C}_2\text{H}_{4.3}\text{ON}_{1.25}$, the ratios approximating closely to those of the compound obtained from ethylic alcohol; hydrogen is liberated in quantity larger than the nitrogen absorbed, but neither carbon oxides nor acetylene is formed.

Ether, with excess of nitrogen, yields a substance, $\text{C}_4\text{H}_{6.4}\text{N}_2\text{O}$, the hydrogen liberated having about double the volume of the nitrogen

absorbed, whilst the latter is practically equal to the volume of the ether in the form of gas.

Most of the products formed in presence of nitrogen are probably closed chain compounds belonging to the pyridine and quinoline groups.

C. H. B.

Formation of Mixed Hydrates of Acetylene and of other Gases. By ROBERT DE FORCRAND and SULLY THOMAS (*Compt. rend.*, 1897, 125, 109—111).—A crystalline mixed hydrate is obtained when pure acetylene gas saturated with carbon tetrachloride vapour is passed into a flask containing small pieces of ice, and kept at 0°. The pressure in the flask is kept at about $1\frac{1}{2}$ atmospheres by making the outlet tube dip under mercury. The crystals are stable at the atmospheric pressure at temperatures below +5°; at higher temperatures they decompose, evolving a considerable quantity of acetylene. The compound is a mixed hydrate of acetylene and carbon tetrachloride, and is more stable than the simple hydrate of acetylene. Similar compounds have been obtained by using chloroform, ethylenic chloride, methylic iodide, bromoform, tribromethane, methylenic chloride, or iodide and methylchloroform. Similar compounds may also be obtained by using ethylene, carbonic anhydride, or sulphurous anhydride in place of acetylene.

J. J. S.

Interaction of Cyanides with Thiosulphates. By LEONARD DOBBIN (*Chem. News*, 1898, 77, 131).—By grinding together potassium cyanide and potassium thiosulphate and leaving them in contact, the change represented by the equation $K_2S_2O_3 + KCN = K_2SO_3 + KCNS$ gradually but completely ensues.

D. A. L.

Dichlorhydrin and Epichlorhydrin. By HUGO FLEMMING (*Chem. Zeit.*, 1897, 21, 97. Compare Abstr., 1896, i, 333).—Dichlorhydrin, and especially epichlorhydrin, are good solvents for different nitrated celluloses, and also for such substances as celluloid. Gun cotton is readily soluble in epichlorhydrin, but even a 20 per cent. solution is so thick that it requires diluting with alcohol before being used as a varnish. It is suggested that these solvents possess several advantages over the usual solvents employed in the nitrated cellulose industries.

J. J. S.

Melibiose. By A. BAU (*Chem. Zeit.*, 1897, 21, 185—188).—The author's determinations of the specific rotatory power of melibiose differ somewhat from those made by Scheibler and Mittelmeier (Abstr., 1890, 1085), but in no case has a crystalline material been obtained, so that even these numbers may not be absolutely correct. The melibiose was obtained from melitriose both by acid inversion and by fermentation. As the result of some 24 determinations $[\alpha]_D = +134.25$, or calculated for the ash-free compound $[\alpha]_D = +136.17$. The strength of the different solutions was calculated in most cases from Brix's table of the specific gravities at 17.5°. Scheibler's number is +126.7—+126.9°, and the fact that it is low is probably due to the formation of decomposition products during the boiling with alcohol.

It has been found that moderately concentrated solutions of melibiose have a higher reduction factor than very concentrated solutions, when the boiling is continued for 4 minutes; when boiled for a longer time, a further quantity of cuprous oxide is precipitated. The factor for 4 minutes is about 90—93 per cent. of that for maltose.

Compounds with calcium, barium, strontium, potassium, and sodium have been prepared; these resemble the corresponding derivatives of milk-sugar. It also resembles milk-sugar in its hydrolysis, it is inverted by hydrochloric, sulphuric, or oxalic acid, but not by lactic, tartaric, or citric acid. For inversion by melibiase, compare *Abstr.*, 1896, i, 453. Melibiose is not fermented by *Saccharomyces cerevisiae*, OF, UF, OS, US; *S. ellipsoideus*, II, Hansen; *S. apiculatus*; *S. Logos* (Van Laer); *Monilia candia*; nor by *Schizosaccharomyces Pombe* (Lindner). Melitriose is not fermented by *Saccharomyces apiculatus*. Melibiose is used technically for determining whether a top yeast is adulterated with a bottom yeast. J. J. S.

Arabinose and Semicarbazide. By WILHELM HERZFELD (*Chem. Centr.*, 1897, ii, 894; from *Zeit. Ver. Rübenzuck.-Ind.*, 1897, 604—605).—When hot solutions of arabinose (1 mol.) and semicarbazide (1 mol.) in 95 per cent. alcohol are mixed, boiled for an hour, and the mixture then evaporated, crystals of *arabinosesemicarbazide*, $C_6H_{13}N_3O_5$, are obtained; this melts and decomposes at 163—164°, is easily soluble in cold water, insoluble in ether, benzene, and chloroform, and dissolves in methylic or ethylic alcohol only on boiling for some time. The rotatory power of an alcoholic solution containing 0.5 gram in 100 c.c. is -0.35° , and of an aqueous solution containing 0.1 gram in 50 c.c. -0.15° . Benzylidenesemicarbazide is obtained by boiling an aqueous solution of arabinosesemicarbazide with benzaldehyde; after filtering, the solution is dextrorotatory. E. W. W.

Effect of Pressure and Temperature on the Conversion of Starch into Sugar. By FRIEDRICH LIPPMANN (*Chem. Centr.*, 1897, ii, 557; from *Österr. Zeit. Zucker-Ind.*, 26, 657—668).—The author describes processes of saccharification carried out under pressures obtained by the use of compressed gases, but at temperatures only slightly above 100°. A number of experiments are described in which pure potato-starch was treated with 3 per cent. of its weight of concentrated sulphuric acid diluted with 10 times its volume of water. Heating was effected by blowing in steam, and the various pressures were obtained by using compressed air, carbonic anhydride, or sulphurous anhydride. The results of 8 experiments showed that as the pressure is increased, the diminution in the time required to effect the conversion becomes relatively less and less, and that the most rapid conversion is obtained when the temperature corresponds to the boiling point of the solution at the given pressure. Rise of temperature has much more effect than increase of pressure, but at temperatures above 120—130° the processes of decomposition and recombination about balance. The best results showed on the average a content of about 96 per cent. of dextrose. Other conditions being similar, pressure has little effect on the purity of the product.

E. W. W.

Action of Diastase on Ungelatinised Starch. By ELEK VON SIGMOND (*Chem. Centr.*, 1897, ii, 614; from *Woch. Brauerei*, 14, 412).—According to the author, the results obtained by Lintner's method (*Woch. Brauerei*, 1890, 22) are uncertain if the mixture is not stirred. From experiments in which a mixture of 2 grams of starch with 50 grams of water and 50 c.c. of malt extract were kept stirred, the author finds that the temperatures of gelatinisation and of solution of potato-starch are identical, namely, 65°; for maize-starch these temperatures are 68° and 70° respectively; for rice-starch, 72° and 83°; for wheat-starch, 62° and 60–65°, and for rye-starch, 55° and 55–60° respectively. When potato-starch is heated with diastase at 65°, 93·06 per cent. is inverted; under similar conditions, 63·5 of maize-starch, 25·3 of rice-starch, 94·26 of wheat-starch, and 91·28 per cent. of rye-starch undergo this change. The author is unable to confirm Lintner's statement with reference to the similarity of the behaviour of maize- and rice-starch, and finds, moreover, that wheat-starch is more readily attacked at 60° than rye-starch. E. W. W.

A New Carbohydrate. Caroubin. By JEAN EFFRONT (*Compt. rend.*, 1897, 125, 38–40).—The grain of *Ceratonia siliqua* has the following composition:—Water, 11·40; nitrogenous matter, 18·92; carbohydrates, 62·00, and fatty matter, 2·3 per cent. The nitrogenous matter is very unequally distributed in the grain. The carbohydrates of the albumen are completely absorbed during germination, whilst those of the spermoderm are not. The carbohydrate of the albumen, for which the author suggests the name *caroubin*, resembles to a certain extent *d*-galactan, but differs from it in its products of hydrolysis; its method of extraction is given in detail. It is a white, spongy, friable substance having the same percentage composition as cellulose. Placed in contact with water, or with normal sodium hydroxide, it forms a jelly or transparent viscid mass, the addition of 3–4 grams of the substance to a litre of water giving the liquid the consistency of a thin syrup. Cold hydrochloric acid dissolves it, but the liquid does not reduce Fehling's solution. With hot nitric acid, it yields levulinic acid. Dilute warm mineral acids hydrolyse the carbohydrate, yielding a dextrogyrate solution which has strong reducing properties.

J. J. S.

Theory of the Sulphite Process and the Constitution of Lignin. By PETER KLASON (*Bied. Centr.*, 1898, 27, 138; from *Svensk kem. tidskr.*, 1897, 9, 135–138).—When coniferin is heated at 108° with calcium hydrogen sulphite, the coniferyl alcohol combines with the sulphite, forming a salt of the dibasic coniferylsulphonic acid. This can only be explained on the assumption that the alcohol of the coniferin contains the group $\text{—CH}_2\cdot\underset{\text{O}}{\text{CH}}\cdot\text{CH}_2$, and the ring being necessarily broken when the sugar is eliminated, an unsaturated compound, or else polymerisation, results.

The behaviour of the lignin of pine wood (lignylglycide) indicates that it is also a glucoside containing an aromatic group. It contains, besides methoxyl, hydroxyl, and active carbonyl groups. The number

of carbon atoms it contains is between 18 and 22. When wood containing lignin is boiled with calcium hydrogen sulphite, the lignylglycide is converted into readily soluble sulphonate, but when the wood is treated with dilute mineral acids, the lignylglycide is converted into a dark-coloured resin containing about 40 carbon atoms.

N. H. J. M.

Methylhydroxyethylamine and Methylhydroxydiethylamine. By LUDWIG KNORR and HERMANN MATTHES (*Ber.*, 1898, 31, 1069—1072. Compare Abstr., 1889, 1218).—Methylhydroxyethylamine and methylhydroxydiethylamine have now been prepared pure by the method previously described (Abstr., 1897, 313). Methylhydroxyethylamine boils at 159° , is a colourless, strongly basic oil, with a characteristic odour, fumes in the air, has a sp. gr. = 0.9370 at $20^{\circ}/4^{\circ}$, and an index of refraction $n_D = 1.4385$ at 20° , and is miscible with water, alcohol, and ether. It yields precipitates with mercuric chloride, phosphomolybdic acid, and potassium bismuthiodide. The *picrate* forms slender, matted needles melting at 148 — 150° ; the *aurochloride* crystallises in anhydrous prisms melting at 145 — 146° , and the *platinochloride* in compact tablets decomposing at 125 — 130° .

Methylhydroxydiethylamine is a thick, colourless, strongly basic oil which fumes in the air, boils at 246 — 248° (corr.) under a pressure of 747 mm., and is miscible with water and alcohol, but is only sparingly soluble in ether. It has a sp. gr. = 1.0377 at $20^{\circ}/4^{\circ}$, and an index of refraction $n_D = 1.4678$ at 20° . It yields precipitates with mercuric chloride, phosphomolybdic acid, tannin, and potassium bismuthiodide. The *picrate* melts at 94 — 95° , and the *aurochloride* at 101 — 102° , whilst the *platinochloride* decomposes at 148 — 150° .

A. H.

Alcohol Bases from Ethylamine. By LUDWIG KNORR and WERNER SCHMIDT (*Ber.*, 1898, 31, 1072—1077).—Ethylene oxide reacts vigorously with ethylamine, forming a mixture of hydroxydiethylamine and dihydroxytriethylamine, which can be separated by fractional distillation. *Hydroxydiethylamine*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\text{Et}$, is a colourless, strongly basic oil, which has a faint odour, and boils at 167 — 169° (corr.) under a pressure of 751 mm., its vapour fuming strongly in the air. It is easily soluble in water, alcohol, and ether, and readily attacks copper and brass, as well as organic tissues. It has a sp. gr. = 0.9140 at $20^{\circ}/4^{\circ}$, and a molecular refraction = 25.66, the index of refraction, n_D , being 1.4440 at 20° . It yields characteristic precipitates with mercuric chloride, phosphomolybdic acid, potassium cadmio-iodide, tannin, and potassium bismuthiodide.

The *hydrochloride* forms lustrous, deliquescent needles, whilst the *aurochloride* crystallises in light yellow needles melting at 127° , and the *platinochloride* forms deliquescent crystals which decompose at about 146° . The *picrate* crystallises in pale yellow, monosymmetric prisms melting at 125 — 127° .

Dihydroxytriethylamine, $\text{NEt}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, is a yellowish oil which has a slight ammoniacal odour, and boils at 251 — 252° (corr.) under a pressure of 750 mm. It is only sparingly soluble

in ether, is very hygroscopic, and readily attacks copper and the epidermis, but has little action on cork; the sp. gr. = 1.0135 at 20°/4°, and the molecular refraction = 36.37, the index of refraction, n_D , being 1.4663 at 20°. The base yields characteristic precipitates with mercuric chloride, phosphomolybdic acid, potassium cadmiiodide, tannin, and potassium bismuthiodide. The *picrate* crystallises in yellow fascicular groups of needles melting at 100—101°. The *hydrochloride* forms deliquescent plates, whilst the *aurochloride* crystallises in light orange-yellow prisms melting at 81°, and the *platinochloride*, $(C_6H_{15}NO_2)_2, H_2PtCl_6 + H_2O$, forms flat, orange-yellow hygroscopic prisms which melt at 49—50°, whereas the anhydrous salt melts at 108—110°. The *ethiodide*, $C_6H_{15}NO_2, EtI$, forms lustrous, thin plates melting at 212—214°. A. H.

Relation of Tervalent to Quinquevalent Nitrogen. By ARTHUR LACHMAN (*Amer. Chem. J.*, 1898, 20, 283—288).—Dimethylnitrosamine and diethylnitrosamine form hydrochlorides which are very unstable salts, readily decomposing at a slightly elevated temperature into nitrosyl chloride and the amine. Diphenylnitrosamine takes up dry hydrogen chloride at ordinary temperatures, with immediate elimination of nitrosyl chloride.

Diethylnitrosamine reacts rapidly with zinc ethyl when heated to 100°, basic gases being given off and tarry matter remaining; but diphenylnitrosamine reacts violently with zinc ethyl to form an amorphous, yellow additive product of unknown composition, melting at about 135°. Water converts it into zinc hydroxide, diphenylamine, and an unstable base which reduces Fehling's solution.

When hydroxylamine acts on diphenylnitrosamine, an additive product is formed which at once decomposes into nitrous oxide and diphenylamine.

It appears that, in all these cases, the quinquevalent nitrogen compound readily splits up into simpler substances containing tervalent nitrogen. A diversity among the attached groups is necessary for the existence of quinquevalent nitrogen, for no compound is known in which all five radicles are alike in chemical character, and all attempts to prepare such a compound have proved abortive. A. W. C.

Diacetonehydroxylamine, and Stereoisomeric Aliphatic Ketoximes. By CARL D. HARRIES and LUDWIG JABLONSKI (*Ber.*, 1898, 31, 1371—1384. Compare this vol., i, 121).—The absence of stereoisomerism among the oximes of unsymmetrical aliphatic ketones has been already the subject of remark (compare Meyer and Scharvin, *Abstr.*, 1897, i, 612), but no satisfactory explanation of the circumstance has been put forward. The authors have found that the oxime of mesitylic oxide is an exception to this rule, being capable of existence in two forms, which probably owe their isomerism to steric influences.

Another ketone having an ethylenic linking in the $\alpha\beta$ -position has been shown to yield isomeric oximes; methylcyclohexenoneoxime, prepared by Hagemann, melts at 88—89° (*Abstr.*, 1893, i, 393), whilst the substance described by Knoevenagel (*Abstr.*, 1895, i, 48) melts at 50—60°. The authors have heated the hydrochloride of the latter

form at 80° , obtaining in this manner the salt of the other modification; they therefore regard the oxime having the higher melting point as the analogue of stable mesityloxime, the more readily fusible derivative corresponding to labile mesityloxime.

Diacetonehydroxylamine, $\text{OH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$, is prepared by the action of hydroxylamine on mesitylic oxide in presence of sodium methoxide, and is purified by conversion into the oxalate; it crystallises from light petroleum, melts at 52° , and boils at $94\text{--}95^{\circ}$ under a pressure of 9—10 mm. The substance is very hygroscopic, dissolving in water and organic solvents; it reduces Fehling's solution immediately when gently heated. The *oxalate*, which crystallises from a mixture of alcohol and ether, and melts at $145\text{--}147^{\circ}$, is extremely soluble in absolute alcohol; the *picrate* melts at $107\text{--}108^{\circ}$, the *hydrochloride* is hygroscopic, and the *platinochloride* and *aurochloride* crystallise slowly in six-sided prisms. The *benzoyl* derivative crystallises in lustrous leaflets, and melts at 165° ; it dissolves in dilute caustic soda, and does not reduce Fehling's solution. The *phenylthiocarbamide* crystallises from light petroleum, and melts at $110\text{--}112^{\circ}$; when gently heated, it reduces Fehling's solution, and when boiled with caustic soda yields mesitylic oxide. Reduction with sodium amalgam converts diacetonehydroxylamine into diacetonealkamine.

β -*Nitrosoisopropylacetone*, $\text{NO}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$, obtained by boiling a solution of diacetonehydroxylamine in chloroform with mercuric oxide in a reflux apparatus, crystallises in stout, white prisms, and melts to a blue liquid at $75\text{--}76^{\circ}$; it is highly volatile, and has a pungent, irritating odour.

Dinitrosodi-isopropylacetone, $\text{CO}(\text{CH}_2\cdot\text{CMe}_2\cdot\text{NO})_2$, is prepared by oxidising triacetonedihydroxylamine under the same conditions; it crystallises from benzene or from toluene, and melts at $132\text{--}133^{\circ}$ to a deep blue liquid.

3 : 5 : 5-*Trimethyldihydroisoxazole*, $\begin{array}{c} \text{CMe} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}\cdot\text{CMe}_2 \end{array} \text{>NH}$, is another pro-

duct of the action of hydroxylamine on mesitylic oxide in presence of sodium methoxide; it is a mobile, highly refractive liquid which boils at 52° and $162\text{--}164^{\circ}$ under pressures of 9 mm. and 760 mm. respectively.

α -*Mesityloxime*, $\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{NOH}$, boils at 85° under a pressure of 10 mm.; it dissolves readily in dilute acids and alkalis, and resists the action of Fehling's solution. The *hydrochloride* is prepared by passing dry hydrogen chloride into an ethereal solution of the fraction of the oxime which boils at $92\text{--}94^{\circ}$, under a pressure of 15 mm., this fraction having been obtained by the action of free hydroxylamine on the ketone; on adding dry ether to the solution in absolute alcohol, it crystallises in regular, four-sided plates. The salt has no definite melting point, but sinters below 55° and melts at about 62° , although solid fragments remain suspended in the liquid at about 70° ; at 80° , it suddenly becomes solid, being converted into the hydrochloride of the stable form.

β -*Mesityloxime* melts at $48\text{--}49^{\circ}$, resembling the labile modification in chemical properties; it boils at 92° and 102° under pressures of 9 mm. and 13 mm. respectively. The *hydrochloride*, prepared in the

manner already described, and also by the action of hydroxylamine hydrochloride on mesitylic oxide, crystallises in long needles, and melts and decomposes at 123° . The salt is produced when a solution of the labilesalt in absolute alcohol is allowed to remain during two days.

The stable modification of methylcyclohexenoneoxime is obtained when hydroxylamine hydrochloride (1 mol.) acts on methylcyclohexenone. When two molecular proportions are employed, the compound, $C_7H_{14}N_2O_2 \cdot H_2O$, is produced; this crystallises from hot water in four-sided prisms, and melts at $83-84^{\circ}$. Its behaviour towards mercuric oxide, which converts it into a deep blue nitroso-derivative, shows the substance to be a hydroxylamino-oxime. M. O. F.

Alkylisocyanates [Carbimides] and Heat of Formation of Liquid Cyanic Acid. By PAUL LEMOULT (*Compt. rend.*, 1898, 126, 43-45).—In the preparation of alkylcarbimides (alkylisocyanates) by Wurtz's method, it is necessary to use potassium cyanate which has been recently prepared, and to take care that all the compounds used are free from water. 100 grams of potassium cyanate and 200 grams of sodium ethyl sulphate give about 12 grams of pure ethylic isocyanate; a quantity of the polymeride is formed at the same time.

Methylcarbimide, $CO \cdot NMe$, is a colourless liquid boiling at 40° , and polymerising with the greatest readiness. The molecular heat of combustion at constant volume is 268.9 Cal., and at constant pressure 269.3 Cal.; the molecular heat of formation at constant pressure is +22.8 Cal. Ethylcarbimide boils at 60° . Its molecular heat of combustion at constant volume is 424.2 Cal., and at constant pressure 424.4; its molecular heat of formation is +31 Cal. It follows from these numbers that the two compounds are true homologues. The heat evolved during polymerisation of methylcarbimide is 34.7 Cal., and for ethylcarbimide 34.9 Cal.; taking the mean of these two numbers, and subtracting it from the heat of formation of cyanuric acid (55.45 Cal.) it gives 20.65 Cal., which should be the heat of formation of liquid cyanic acid. J. J. S.

Bromacraldehyde and Tribromopropaldehyde. By OSCAR PILOTY and ALFRED STOCK (*Ber.*, 1898, 31, 1385-1388).—*Bromacraldehyde*, $CH_2 \cdot CBr \cdot CHO$, prepared by the action of a boiling, aqueous solution of sodium acetate on dibromopropaldehyde, is a colourless, mobile liquid having an intensely irritating smell, and gradually undergoes decomposition with development of a yellow coloration. The substance boils at 28.5° , 37° , 49° , and 111° (corr.), under pressures of 11 mm., 14 mm., 27 mm., and 420 mm. respectively, slowly undergoing decomposition when distilled under atmospheric pressure; it has the sp. gr. = 1.68. The aldehyde is neutral to litmus, and dissolves somewhat readily in warm water, more sparingly, however, in cold; it reduces Fehling's solution vigorously when heated.

Tribromopropaldehyde, $CH_2Br \cdot CBr_2 \cdot CHO$, is the product of the action of bromine on the foregoing substance; it has the sp. gr. = 2.51, and remains unchanged when protected from light, which turns it yellow. It boils at 85.5° (corr.) under a pressure of 11 mm., but under atmospheric pressure it decomposes above 155° , yielding

hydrogen bromide. The aldehyde dissolves with difficulty in cold water, but is miscible with ether, benzene, methylic alcohol, and ethylic alcohol, generating heat with the latter. When exposed to air, it absorbs moisture, yielding the *hydrate* which contains $2\text{H}_2\text{O}$ and crystallises from water in large rhombic plates; it melts at $55-57^\circ$, and reduces Fehling's solution when heated. M. O. F.

A New Cyclic Ketone. Δ^6 -Methylcyclohexenone-3. By AUGUSTE BÉHAL (*Compt. rend.*, 1898, 126, 46—49).—The benzoyl derivative, melting at 167° , from the ketone isolated from wood oil, when treated with alkalis, gives an oxime melting at 121.5° , and this, on hydrolysis with hydrochloric acid, yields a *ketone*, $\text{C}_7\text{H}_{10}\text{O}$, boiling at 192° and melting at 12° . It does not combine with sodium hydrogen sulphite, or yield iodoform on treatment with iodine and alkalis. In carbon bisulphide solution, it readily combines with bromine, yielding a *dibromide* which is easily soluble in warm alcohol or light petroleum. The ketone reacts with phosphorus pentachloride, yielding a deep greenish-blue liquid, which, when distilled in steam, yields a small quantity of a heavy oil with an odour resembling that of terebenthene, a small quantity of a crystalline product and the regenerated ketone. When oxidised with permanganate, the ketone yields acetic and levulinic acids only. The author considers these reactions best agree with the formula for the ketone, $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{CH}_2$.

J. J. S.

Alkylic Salts of Chlor- and Brom-acetic Acid. By RUDOLF L. STEINLEN (*Chem. Centr.*, 1897, ii, 659; from *Bul. Acad. roy. Belg.*, [iii], 34, 101—108).—*Propylic chloracetate* is an oil of an ethereal odour, of sp. gr. = 1.0944 at $15^\circ/4^\circ$, and boils at 149° . *Butylic chloracetate* is a colourless liquid of sp. gr. = 1.0675 at $15^\circ/4^\circ$, boils at 170° , and has an odour similar to the preceding salt. *Propylic bromacetate* is a colourless liquid which soon becomes dark, has a sp. gr. = 1.4166 at $15^\circ/4^\circ$, and 1.4099 at $20^\circ/4^\circ$, and boils at 178° under 765 mm. pressure; its vapour, like that of the following salts, has a very irritating action on the eyes. *Isopropylic bromacetate* is a yellowish oil, of sp. gr. = 1.399 at $15^\circ/4^\circ$, and boils at 165.5° under 769 mm. pressure. *Iso-butylic bromacetate* is a yellowish oil which rapidly becomes dark, boils at 188° under 752 mm. pressure, and has sp. gr. = 1.3327 at $15^\circ/4^\circ$, = 1.3269 at $20^\circ/4^\circ$. All these substances are insoluble in water and soluble in alcohol and ether.

A table is given showing how the substitution of chlorine by bromine in the analogous alkylic salts of chloracetic or bromacetic acid raises the boiling point regularly by $16-18^\circ$. E. W. W.

Effect of Temperature on the Acidity of Acids. By PAUL DEGENER (*Chem. Centr.*, 1897, ii, 936; from *Festschrift Techn. Hochschule Braunschweig*, 1897, 451—464).—When asparagine is titrated with normal alkali in the cold, using unneutralised phenolphthalein as indicator, only 0.264 equivalent of alkali is required for each molecule of acid, and if the solution is then heated to 100° , a further quantity of 0.540 equivalent of alkali is necessary to neutralise the solution. If the solution is heated to 100° before titrating, 0.96 equi-

valent of alkali is required, and, on cooling, the solution becomes alkaline, and, when cold, 0.69 equivalent of sulphuric acid must be added to destroy the red coloration. Ammonia is not liberated when the solutions are heated, and the author attributes this change in acidity to the decomposition of more complex molecules, and not to the hydrolysis of the asparagine. Aspartic acid requires 0.94 equivalent of alkali at 0°, and 1.208 at 100°; the hot neutralised solution becomes alkaline on cooling, and, "after neutralising the excess required 1.024—1.058 equivalents of alkali." (?) To neutralise sulphurous acid in the cold, 15.6 per cent. more alkali than is necessary to form K_2SO_3 must be added, and, when heated, the solution becomes alkaline. According to the author, orthosulphurous acid, $S(OH)_4$, is present in the cold solution, and this, when the solution is warmed, decomposes into sulphurous acid and water.

Butyric acid at 0° takes up 97.9, and at 100°, 98.55 per cent. of the calculated amount of alkali; the change of colour is sharp, as is generally the case with acids which contain no hydroxyl groups. Acetic and oxalic acids combine with the theoretical quantity of alkali, both in the cold and when heated. Glutaric acid requires 77—77.5 c.c., and succinic acid, both at 0° and at 100°, 101.7 c.c., instead of 100 c.c. Lactic acid at 0° takes up only sufficient alkali to combine with the carboxyl groups, but, at 100°, 9—12 per cent. more is used. Malic acid requires 93.4 c.c. in the cold, and 95.0 c.c. at 100°, instead of 92.0 c.c., and tartaric acid, when warmed, requires 101 c.c. instead of 100 c.c. In the case of these hydroxy-acids, and also of citric acid, probably some alkali is used to combine with the hydroxyl groups. When tartaric acid is dried at 100°, and a solution of it then at once titrated, only 60 c.c. of alkali are required in the cold, and 89.5 c.c. when heated. According to the author, this is due to the formation, without loss of weight, of an internal anhydride, which is only slowly hydrolysed. Citric acid dried at 100° behaves in a similar way. Phosphoric acid in the cold combines with 63 per cent. of the alkali necessary to form the tribasic phosphate. E. W. W.

δ-Amidovaleric Acid. By HEINRICH SALKOWSKI (*Ber.*, 1898, 31, 776—783).—A sample of δ-amidovaleric acid obtained in the putrefaction of glue was compared with a sample prepared synthetically by oxidising benzoylpiperidine with potassium permanganate, and hydrolysing the product with hydrochloric acid (Schotten, *Abstr.*, 1888, 1104), and with another obtained years before (*Abstr.*, 1883, 925) in the putrefaction of fibrin and flesh. The aurochlorides had the same melting point and crystalline form [monoclinic; $a:b:c = 1.1756:1:1.0043$; $\beta = 48^\circ 23' 40''$]; the benzoyl derivatives melt at the same temperature, which is 105.1° , as determined by a thermometer immersed in the solidifying substance.

When the orange aurochloride, $C_5H_{11}NO_2 \cdot HAuCl_4 + H_2O$, is recrystallised from water, a yellow salt, with the unusual composition $C_5H_{11}NO_2 \cdot AuCl_3$, is obtained; this can also be obtained, although with difficulty, by the direct combination of $AuCl_3$ with amidovaleric acid. Recrystallisation from dilute hydrochloric acid reconverts it into the original aurochloride. C. F. B.

Use of Zinc Oxide in the Preparation of Fermentation Lactic Acid. By JOHANNES GADAMER (*Chem. Centr.*, 1897, ii, 937; from *Apoth.-Zeit.*, 12, 642—643).—The author attributes Kassner's failure to obtain lactic acid by fermenting a solution of sugar in presence of zinc oxide (this vol., i, 296) to his using a large quantity of old cheese, which does not induce energetic fermentation, instead of sour milk, which contains abundant lactic acid bacteria. When the latter is employed, zinc dextrolactate is obtained. Calcium carbonate, which Kassner used instead of zinc oxide, is probably a favourable material for the growth of lactic acid bacteria. Commercial lactic acid is either inactive or dextrorotatory. E. W. W.

Autoracemisation. By PAUL WALDEN (*Ber.*, 1898, 31, 1416—1422. Compare this vol., i, 178).—The author has repeatedly shown that, under the influence of heat, the specific rotatory power of halogen substituted ethereal salts readily undergoes change. Data are collected in the present paper showing that compounds of a certain class exhibit diminution of rotatory power after lapse of time, without being submitted to external influences. Of the compounds which have been examined, methylic *d*-bromosuccinate, ethylic *d*-bromosuccinate, isopropylic *d*-bromosuccinate, isobutylic *d*-bromosuccinate, methylic *d*-phenylbromacetate, isobutylic *d*-phenylbromacetate, and *d*-phenylbromacetic acid exhibit this phenomenon, which, however, is not shown by propylic *d*-bromosuccinate, methylic *d*-chlorosuccinate, isopropylic *d*-chlorosuccinate, methylic acetylmalic acid, ethylic isobutyrylmalic acid, methylic *d*-chloropropionate, ethylic *d*-phenylchloracetate, ethylic *l*-mandelate, and ethylic isovaleryl-*l*-mandelate.

The author recognises the following points.

1. There exist active compounds, particularly bromine substituted compounds of succinic, propionic, and phenylacetic acids, which exhibit a decrease of rotational activity if kept for a considerable period; in some cases, the rotatory power is completely lost, and the change in question is associated with both liquid and solid states.

2. The diminution or loss of activity is spontaneous, and proceeds without decomposition on the part of the active substance, the composition, and such physical constants as boiling point, density, and refractive index, undergoing no change.

3. The alteration is permanent, and neither fractionation nor crystallisation of the product is capable of restoring the original rotation.

4. The phenomenon depends on the structure of groups which enter compounds of the same type, shown by the difference in behaviour of propylic and isopropylic *d*-bromosuccinates; it is also associated with the nature of the four groups attached to the asymmetric carbon atom, being non-existent in the case of hydroxy-compounds, hardly recognisable among chloro-derivatives, although well defined in the case of bromo-compounds. M. O. F.

Partial Racemism. By ALBERT LADENBURG and W. HERZ (*Ber.*, 1898, 31, 937—938).—The solubility of the quinine salt of *l*-pyrotartaric acid in alcohol has now been determined, and it has been found that 100 parts of alcohol dissolve 15 parts of this compound, 4.2 parts of the salt of the dextro-acid, and 3.2 parts of the salt of the inactive

acid. From this it follows that the salt of the inactive acid is not a mixture of the salts of the dextro- and lævo-acids, but is an individual salt derived from the racemic acid.

A. H.

A Method of Preparing Ethylic Alkylideneacetoacetates. By EMIL KNOEVENAGEL (*Ber.*, 1898, 31, 730—737).—It has been shown that benzaldehyde (1 mol.) will react at a low temperature with ethylic acetoacetate (1 mol.), under the influence of a little piperidine, forming ethylic benzylideneacetoacetate, $\text{CHPh}:\text{CAc}\cdot\text{COOEt}$ (*Abstr.*, 1896, i, 232). This will react with a second molecule of ethylic acetoacetate, yielding ethylic benzylidenediacetoacetate, $\text{CHPh}(\text{CHAc}\cdot\text{COOEt})_2$ (Hantzsch, *Abstr.*, 1886, 77; Knoevenagel, *Abstr.*, 1896, i, 210). More examples of these reactions have been investigated, both aromatic and aliphatic aldehydes being used. The aldehyde and ethylic acetoacetate were usually mixed at -10° to -15° , a small quantity of piperidine was added, one drop at a time and at intervals of several minutes, and the mixture was then allowed to remain at the same temperature, sometimes for a day or two. In some cases the product crystallised out; if it did not, the mixture was washed with dilute sulphuric acid (to remove piperidine) and then with water, dried over dehydrated sodium sulphate, and distilled under diminished pressure. The aldehydes experimented with were cuminaldehyde, orthonitrobenzaldehyde, salicylaldehyde, furfuraldehyde, cinnamaldehyde, acetaldehyde, isobutyraldehyde, isovaleraldehyde, and cenanthaldehyde. Most of the acetoacetates had been obtained before by the use of other condensing agents, such as acetic anhydride or hydrochloric acid; the diacetoacetates obtained were also known previously.

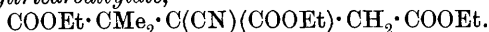
The following compounds, or boiling points, are new, however. *Ethylic cumylideneacetoacetate*, boiling at 198° under 10 mm. pressure. *Ethylic cinnamylideneacetoacetate*, boiling at $213\text{--}214^\circ$ under 17 mm. pressure. *Ethylic cenanthylideneacetoacetate*, boiling at 145° under 10 mm. pressure, and with sp. gr. = 0.9647 at 21° . Acetylcoumarin is the product when salicylaldehyde is used; it, as well as its phenylhydrazone (the hygroscopic sodium salt of which melts at 160°) and oxime were described (Arnot, *Inaug.-Diss.*, Heidelberg, 1896) before the publication of Rap's results (*Gazzetta*, 1897, 27, ii, 498; this vol., i, 317). Ethylic ethylideneacetoacetate boils at 107° , 101° , 96° , and 94° under pressures of 20, 15, 11 and 9 mm. respectively. Ethylic isobutylideneacetoacetate boils at $118\text{--}124^\circ$ under 12 mm., ethylic isoamylideneacetoacetate at $136\text{--}138^\circ$ under 9 mm. pressure, and has a sp. gr. = 0.9623 at 21.5° .

C. F. B.

Syntheses by the Aid of Ethylic Cyanosuccinate. By LÉONCE BARTHE (*Compt. rend.*, 1897, 125, 182—183).—A mixture of sodium (3.45 grams), alcohol (150 c.c.), and ethylic cyanosuccinate (30 grams) is added to trimethylenic bromide, and the mixture heated in a reflux apparatus for 5 hours on the water bath. After distilling off the alcohol, the residue is well washed with water and purified by distillation under diminished pressure, or by crystallising from alcohol. The product, *ethylic $\beta\beta_1$ -dicyanoheptane-aa, $\beta\beta_1$ -tetracarboxylate* (3:7-dicyanononanedioate-3:7-dimethylate), $\text{CH}_2[\text{CH}_2\cdot\text{C}(\text{CN})(\text{COOEt})\cdot\text{CH}_2\cdot\text{COOEt}]_2$,

crystallises in white, silky crystals melting at 69° and boiling at 215° under 75 mm. pressure.

When a solution of sodium (2.9 grams) in absolute alcohol is mixed with ethylic cyanosuccinate (25 grams), then added to ethylic α -bromoisobutyrate (24 grams), and the reaction completed by heating for 3 hours on the water bath; the product isolated as described above is a colourless oil boiling at 233 — 235° under 25 mm. pressure, and is *ethylic cyanodimethyltricarballylate*,



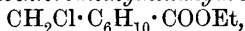
J. J. S.

The Naphthenes of Russian Petroleum. By OSSIAN ASCHAN (*Chem. Zeit.*, 1897, 21, 242, and 287—288).—A *résumé* of work previously published by the author and others. Compare Abstr., 1883, 564; 1884, 1276; 1887, 648, 922; 1891, 1053, 1481; 1892, 847, 1182, 1310, 1311; 1895, i, 339, 411, and 1896, i, 210, 286, 350.

The conclusion arrived at is that these naphthenes are probably mixtures, and they are not, as was previously supposed, reduction products of benzene hydrocarbons but probably contain pentamethylene derivatives.

J. J. S.

Reduction of Benzylaminocarboxylic Acids. By ALFRED EINHORN [and JOSEF BRANTL] (*Annalen*, 1898, 300, 156—179. Compare Abstr., 1896, i, 551).—*Orthomethylolhexahydrobenzoic acid* (*exo-hydroxyhexahydro-orthotoluic acid*), $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_{10} \cdot \text{COOH}$, is the chief non-nitrogenous product of reducing orthodiethylbenzylaminocarboxylic acid with amyl alcohol and sodium, and is also obtained by the reduction of phthalide; it crystallises from benzene in aggregates of small, prismatic needles, and melts at 112° . The *sodium* and *barium* salts crystallise in needles, the *methylic* salt boils at 155° under a pressure of 18 mm., and the *ethylic* salt at 160 — 162° under a pressure of 32 mm. *Ethylic orthochloromethylhexahydrobenzoic acid*,



boils at 145 — 147° under a pressure of 15 mm. When oxidised with potassium permanganate, orthomethylolhexahydrobenzoic acid is converted into *trans*-hexahydrophthalic acid.

In addition to *exo*-hydroxyhexahydro-orthotoluic acid, reduction of phthalide gives rise to *hexahydrophthalide*, $\text{C}_6\text{H}_{10} \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{O}$; it is a colourless liquid having an agreeable odour, and it boils at 160 — 165° under a pressure of 60 mm.

Hexahydro-orthotoluic acid is another product of the reduction of phthalide and *exo*-hydroxyhexahydro-orthotoluic acid, and when distilled with zinc chloride, it yields hexahydrotoluene.

M. O. F.

Compound of Phosphoric Anhydride with Benzene. By H. GIRAN (*Compt. rend.*, 1898, 126, 592—593).—When a mixture of two parts of phosphoric anhydride and three parts of benzene is heated in a sealed tube at 110 — 120° for several hours, a very unstable, brick-red solid product is obtained which decomposes when exposed to air, but can be kept in an atmosphere of benzene. It is also decomposed

by water, but dissolves without change in alcohol, and when this solution is treated with barium carbonate, a gelatinous mass is formed which, after washing with absolute alcohol and drying at 110—120°, has the composition $C_6H_2P_8O_{20}Ba_2$, and is the barium salt of *benzenetetradimetaphosphoric acid*, $C_6H_2(PO:O_2:PO:OH)_4$, formed by the union of 1 molecule of benzene with 4 mols. of phosphoric anhydride.

The alcoholic solution of the crude acid may be neutralised with barium ethoxide instead of with the carbonate. C. H. B.

The Benzene Ring. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1898, 31, 1423—1429. Compare this vol., i, 186).—A study of the formation of the benzene ring involves the consideration of two questions, namely, the production of a hexatomic ring from an open chain, and the influence on the decomposition velocity of the anilines exerted by the carbon linkings of the ring.

In order to throw light on the first of these questions, the author has compared the velocity constants of the action of allylic bromide on α -pentylamine (1189), hexamethyleneamine (1309), $\alpha\beta$ -pentylamine (586), and β -methylhexamethyleneamine (884), and points out that the conversion of an open chain into a hexatomic ring having the same simple linkings between the carbon atoms is not attended with diminution of the velocity constant.

Assuming that the influence exerted by the nature of the union between carbon atoms is the same in a closed ring as in an open chain, it is possible to study the second of the above questions by considering the velocity constants of the anilines. By comparing the velocity constants of propylamine (3783) and allylamine (1903), it will be seen that if Kekulé's formula for benzene is accepted, the constant for aniline should be considerably lower than that of hexamethyleneamine; the same effect would be anticipated if Claus' view of the structure of the benzene ring is accepted, because the velocity constant of $\alpha\alpha$ -pentylamine is 270. As a matter of fact, the constants proper to hexamethyleneamine and aniline are 1309 and 68 respectively. Another point of difference which is due to this cause lies in the lower values obtained when anilines are acted on by methylic bromide as compared with allylic bromide, whereas in the aliphatic series the converse generalisation holds good; this is illustrated by the following table (compare also Abstr., 1895, ii, 385).

	$C_3H_5Br.$	MeBr.
Aniline	68	24
Methylaniline	504	179
Orthotoluidine	54	13
Metatoluidine	445	86
Paratoluidine.....	96	52
<i>v</i> -Ortho-xylidine	400	51
<i>as</i> -Meta-xylidine	235	30
ψ -Cumidine	174	46

The aromatic amines, such as benzylamine, differ from the anilines,

displaying the characteristics of aliphatic amines to the exclusion of those features which are associated with the benzene ring. Thus the velocity constants of benzylamine, α -phenylethylamine, and ω -mesitylamine, with allylic bromide, are 997, 750, and 1718; with methylic bromide, the constants of benzylamine and ω -mesitylamine are 2722 and 4565 respectively.

Corresponding differences are revealed on comparing the etherification constants of alcohols with those of phenols, and of aliphatic acids with those of aromatic acids.

M. O. F.

Carbonates of the Dihydroxybenzenes. By ALFRED EINHORN [and EUGEN LINDENBERG] (*Annalen*, 1898, 300, 135—155).—When catechol carbonate, $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} CO$, is recrystallised from absolute alcohol, it becomes in part converted into ethylic catechol carbonate, $OH \cdot C_6H_4 \cdot O \cdot COOEt$. It is also decomposed by primary and secondary bases, yielding compounds of the type $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NRR_1$. Whilst ethylenediamine gives rise to dicaticholdicarbethylenediamide, $C_2H_4(NH \cdot CO \cdot O \cdot C_6H_4 \cdot OH)_2$, hydrazine forms the two compounds dicaticholcarbohydrazide, $N_2H_2(CO \cdot O \cdot C_6H_4 \cdot OH)_2$, and catecholcarbohydrazide, $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NH \cdot NH_2$. The latter is of value in detecting aldehydes, with which it forms derivatives of the type $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NH \cdot N \cdot CHR$, and possesses the advantage of solubility in alkalis, from which it is separated unchanged by acids; hitherto, however, it has not been induced to combine with ketones, and therefore affords a means of distinguishing between this class of compounds and aldehydes.

Although the conversion of catechol carbonate into ethylic catechol carbonate under the influence of absolute alcohol is complete at 100° , the carbonates of resorcinol and quinol are scarcely changed under these conditions, first undergoing complete conversion when heated at 130° and 160° respectively; the products, however, have not been isolated. With piperidine, resorcinol carbonate yields two compounds, resorcinolcarbopiperidide, $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NC_5H_{10}$, which dissolves in alkalis, and resorcinoldicarbodipiperidide, $C_6H_4(O \cdot CO \cdot NC_5H_{10})_2$, which is insoluble in alkalis. Quinol carbonate behaves in a similar manner.

It is probable that the carbonates of resorcinol and quinol are not monomolecular, and the authors therefore represent them by the general formula $(C_6H_4O_2 \cdot CO)_x$.

Ethylic catecholcarbonate, $OH \cdot C_6H_4 \cdot O \cdot COOEt$, crystallises from a mixture of alcohol and ether in colourless needles and melts at 58° ; it has an aromatic odour and a burning taste, and does not develop colour with ferric chloride. Distillation regenerates catechol carbonate with elimination of alcohol.

Allylic catechol carbonate, $OH \cdot C_6H_4 \cdot O \cdot COO \cdot C_5H_{11}$, crystallises from petroleum in leaflets and melts at 53° ; it has an aromatic odour.

Catecholcarbanilide, $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NHPh$, crystallises from alcohol in small, white scales, and melts at 146° . *Catecholcarboparaphenetidide*, $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NH \cdot C_6H_4 \cdot OEt$, crystallises in lustrous leaflets and also melts at 146° .

Catecholcarbophenylhydrazide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$, slowly reduces a cold solution of silver nitrate, and is oxidised by Fehling's solution when gently heated; it crystallises from methylic alcohol in leaflets and melts at 157° .

Dicatecholcarbethylenediamide, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$, is prepared by the action of ethylenediamine on catechol carbonate (2 mols.); it crystallises from absolute alcohol in highly lustrous leaflets and melts at 165.5° .

Catecholcarbodiethylamide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{N} \cdot \text{Et}_2$, which crystallises in beautiful prisms from a mixture of ether and petroleum, melts at 78° , and dissolves without decomposition in dilute caustic soda. It belongs to the monoclinic system. [$a:b:c = 1.2261:1:0.95498$; $\beta = 114^\circ 26'$.]

Catecholcarbopiperidine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NC}_5\text{H}_{10}$, crystallises from absolute alcohol in white prisms and melts at 121° . When boiled with alcohol during half an hour, it is resolved into its components, but dissolves without change in cold, dilute, caustic alkali.

Dicatecholcarbohydrazide, $\text{N}_2\text{H}_2(\text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$, is prepared by adding hydrazine (2.8 grams) to finely powdered catechol carbonate (15 grams), and cooling the clear solution which is produced; on dissolving the crystals in dilute caustic soda, and treating the filtered liquid with hydrochloric acid, the dihydrazide is precipitated, whilst the hydrochloride of the monohydrazide remains in solution. The dihydrazide crystallises from absolute alcohol in colourless plates and melts at 207° .

Catecholcarbohydrazide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, crystallises from very dilute spirit in white needles, and melts at 154° , becoming solid above this temperature, and finally decomposing at 240° ; it is insoluble in benzene and ether, but dissolves in hot alcohol and water. The substance slowly reduces a cold solution of silver nitrate and Fehling's solution when warmed with it; ferric chloride develops a dark coloration. The *acetyl* derivative melts at 180° . The *benzylidene* derivative crystallises from alcohol in colourless needles and melts at 175° ; the *orthohydroxybenzylidene* and *parahydroxybenzylidene* derivatives melt at 162° and 175° respectively, the *paramethoxybenzylidene* derivative at 192° . The *ethylidene* derivative melts at 125° ; unlike the foregoing products of condensation, this compound undergoes decomposition when dissolved in alkalis.

Resorcinol carbonate, $(\text{C}_6\text{H}_4\text{O}_2 \cdot \text{CO})_x$, is prepared by passing carbonyl dichloride into a continuously agitated solution of resorcinol in pyridine, cooled with ice; after half an hour the gelatinous precipitate is transferred to water, when the carbonate separates as a white, amorphous powder. It melts and evolves gas at 190° .

Resorcinoldicarbopiperidide, $\text{C}_6\text{H}_4(\text{O} \cdot \text{CO} \cdot \text{NC}_5\text{H}_{10})_2$, separates in large, transparent plates on adding a few drops of alcohol to the solution in ether; it melts at 122° . *Resorcinolcarbopiperidide*,

$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NC}_5\text{H}_{10}$, is soluble in alkalis, and crystallises from a mixture of ether and petroleum in colourless prisms. It melts at 107° .

Quinol carbonate, $(\text{C}_6\text{H}_4\text{O}_2 \cdot \text{CO})_x$, is insoluble in common solvents and does not melt below 280° .

Quinolcarbopiperidide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NC}_5\text{H}_{10}$, which separates on adding ethylic acetate to the alcoholic or ethereal solution, melts at 270° .

Quinolcarbohydrazide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, is a white, crystalline powder and melts at 168° . M. O. F.

Action of Cyanamide on Bromanil in Presence of Potassium Hydroxide. By H. IMBERT (*Compt. rend.*, 1898, 126, 529—530).—A solution of cyanamide (8.4 grams), in water (100 grams), is added to finely divided tetrabromoquinone (24.6 grams), the mixture is boiled, and small pieces of potassium hydroxide are added, care being taken that the bromanil remains in excess; the liquid is filtered hot, and as the filtrate cools crystals separate which can be obtained pure after two or three crystallisations from boiling water. The crystals have the form of long needles, some have a green and others a brown appearance, probably the effect of polychroism. Its aqueous solution has a green colour, which changes to violet on the addition of hydrochloric acid; if the acidified solution is shaken with ethylic acetate, the latter assumes a ruby-red colour. Both the green and violet solutions are decolorised by sulphurous anhydride. Analyses point to the compound being *dipotassium dicyanimidodibromdihydroxyquinone*, $\text{CN}_2 \cdot \text{C}_6\text{Br}_2(\text{OK})_2 \cdot \text{CN}_2 + 2\text{H}_2\text{O}$. The corresponding *silver* and *barium* compounds have been obtained by double decomposition. Chloranil reacts in a similar manner, and benzoquinone itself gives dicyanimido-benzoquinone. J. J. S.

Veratrylenediamine. By CHARLES MOUREU (*Compt. rend.*, 1897, 125, 31—34).—Veratrole, when treated at $0-5^\circ$ with concentrated nitric acid (sp. gr. = 1.48), yields a *dinitro*-derivative crystallising in lemon-yellow needles and melting at $129-130^\circ$. The two nitro-groups appear to be in the ortho-position relatively to one another, since on reduction with tin and hydrochloric acid an orthodiamine, *veratrylenediamine*, $\text{C}_6\text{H}_2(\text{OME})_2(\text{NH}_2)_2$, is obtained; this crystallises in small, colourless prisms melting at $131-132^\circ$, and dissolves readily in water, alcohol, or chloroform, but is only sparingly soluble in ether. All its solutions rapidly become dark coloured on exposure to the air, and even the solid base after exposure for several hours assumes a violet colour.

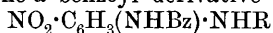
Veratrylphenanthrazine, $\text{C}_6\text{H}_2(\text{OME})_2 \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{smallmatrix}$, obtained when a warm alcoholic solution of the base (0.84 gram) is added to a boiling acetic acid solution of phenanthraquinone (1.04 grams), crystallises from toluene in small, yellow needles melting at 255° , and gives a violet coloration with sulphuric acid.

Veratrylene-ethenylamidine, $\text{C}_6\text{H}_2(\text{OME})_2 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CMe}$, formed when the base is heated for some time with acetic acid, is readily soluble in water, sparingly in ether, and melts at about 170° ; its aqueous solution yields precipitates with both platinum chloride and picric acid.

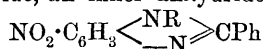
Veratrylbenzaldehydine, $\begin{smallmatrix} \text{CPh} \cdot \text{N} \cdot \text{CH}_2\text{Ph} \\ | \\ \text{N} - \text{C}_6\text{H}_2(\text{OME})_2 \end{smallmatrix}$, is obtained in the form of its hydrochloride when an aqueous solution of veratrylenediamine hydrochloride reacts with benzaldehyde; the *hydrochloride* crystallises

from dilute alcohol in small, colourless needles melting at 134—135°. All these reactions indicate that the base is an ortho-diamine. J. J. S.

Action of Benzoic Chloride on Monosubstituted Orthodiamines. By FERNAND MUTTELET (*Compt. rend.*, 1897, 125, 107—109).—Substituted ortho-diamines of the type $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2)(\text{NHR})$ [$\text{NHR} : \text{NH}_2 = 1 : 2 : 4$], where R = phenyl, ortho- or para-tolyl, methyl, α - or β -naphthyl radicles, react with benzoic chloride in two different ways. (1) At a low temperature and in the presence of a solvent such as benzene a benzoyl derivative of the type



is formed. (2). At a high temperature (200°), and in the presence of an excess of the chloride, an inner anhydride of the type



is produced.

Orthobenzamidoparanitrophenylaniline, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NHBz}) \cdot \text{NPh}$, crystallises from alcohol in yellowish brown needles melting at 201—202°. *Orthobenzamidoparanitroparatolylaniline* forms yellow needles melting at 210—211°; *orthobenzamidoparanitroorthotolylaniline* melts at 164—165°, and *orthobenzamidoparanitro- β -naphthylaniline* melts at 217—218°.

The *anhydride*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \underset{\text{—N}}{\text{NPh}} > \text{CPh}$, is obtained when paranitro-orthamidophenylaniline (1 part) is heated with benzoic chloride (2 parts), first gently and then at about 210—215°, in an oil bath until hydrogen chloride ceases to be evolved; when cold, the mass is treated with sodium carbonate, and, after boiling, the insoluble portion is washed with hot water and recrystallised from boiling alcohol; it crystallises in needles melting at 181°.

The following is a list of the anhydrides which have been obtained in a similar manner.

R = Paratolyl, colourless needles melting at 177—178°.

R = Orthotolyl, yellowish needles melting at 172—173°.

R = α -Naphthyl, small yellow crystals melting at 171—173°.

R = β -Naphthyl, yellow needles melting at 177—178°.

R = Methyl, yellow crystals melting and decomposing at 140°.

J. J. S.

A New Group of Amidines. By FERNAND MUTTELET (*Compt. rend.*, 1897, 125, 243—245).—When the anhydrides obtained by the action of benzoic chloride on monosubstituted orthodiamines (see preceding abstract) are reduced with tin and hydrochloric acid, amidines of the type $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \underset{\text{—N}}{\text{NR}} > \text{CPh}$ are formed.

R.	Melting point of product.
Phenyl	191°
Paratolyl	193°
Orthotolyl.....	145—146°
β -Naphthyl	195°

A hydrate of the phenyl derivative containing $1\text{H}_2\text{O}$ has been obtained, it melts at 172—173°; the corresponding hydrate of the

β -naphthyl derivative melts at 165—166° losing its water and then melting again at 195°. J. J. S.

Behaviour of Diazomethane towards Nitramines and Aromatic Nitro-compounds. By JOHN LEATHART HEINKE (*Ber.*, 1898, 31, 1395—1400. Compare Degner and von Pechmann, *Abstr.*, 1897, i, 264).—Diazomethane converts nitrourethane into nitromethylurethane. It has a similar action on nitramine, yielding principally dimethylnitramine, along with the isomeride described by Franchimont and Umbgrove (*Abstr.*, 1897, i, 8); there is also formed the *compound*, $C_5H_{11}NO_4$, which boils at 110—112°, and yields potassium carbonate when treated with alcoholic potash.

The nitro-compounds which have shown themselves to be indifferent towards diazomethane are nitromethane, nitrobenzene, nitrotoluene, parabromonitrobenzene, bromodinitrobenzene, and trinitromesitylene.

Symmetrical trinitrobenzene reacts with diazomethane (4 mols.) liberating nitrogen, and yielding the *compound*, $C_{10}H_{11}N_5O_6$, which crystallises from dilute acetic acid in colourless, rhombic plates, and melts at 194—195°, when it decomposes; it is indifferent towards cold caustic soda, yielding a red solution when the liquid is boiled. The substance gives Liebermann's reaction, and under the influence of acids and alkalis is resolved into nitrous acid and the *base*, $C_{10}H_{10}N_4O_4$, which crystallises from dilute alcohol in white, lustrous plates and melts at 164—165°.

Symmetrical trinitrotoluene yields the *compound*, $C_{10}H_{11}N_5O_6$, which crystallises from dilute acetic acid in yellowish needles, and melts at 177°.

Picric chloride gives rise to the *compound*, $C_9H_8N_5O_6Cl$, which crystallises from dilute acetic acid in bright yellow needles, and melts at 176—177°. Alcoholic hydrogen chloride eliminates nitrous acid, yielding the *base*, $C_9H_7N_4O_4Cl$, which crystallises from dilute alcohol in yellowish needles and melts at 179—180°; the *acetyl* derivative forms colourless needles and melts at 156—157°.

Symmetrical trinitrophenylic acetate acts readily with diazomethane, yielding the *compound*, $C_{11}H_{11}N_5O_7$, which separates from dilute acetic acid in yellowish, hexagonal prisms; it melts at 144°. M. O. F.

Compounds of Phenylhydrazine with Metallic Nitrates. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, 125, 183—185).—The nitrates of metals of the manganese series combine directly with phenylhydrazine in much the same manner as the corresponding haloids (*Abstr.*, 1897, i, 561, 562; this vol., i, 133). These salts, which give the reactions of phenylhydrazine, and also those of the metal they contain, deflagrate when heated, leaving a residue of the metallic oxide.

Cobalt nitrate phenylhydrazine, $Co(NO_3)_2 \cdot 2N_2H_3Ph + H_2O$, obtained when an excess of phenylhydrazine is quickly added to a 10 per cent. aqueous solution of cobalt nitrate previously diluted with twice its volume of 95 per cent. alcohol, crystallises in microscopic needles, is sparingly soluble in cold water or alcohol, more readily in hot water, and insoluble in ether or chloroform. When heated, it turns blue, then brown, and does not melt below 260°.

Zinc nitrate phenylhydrazine, $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{N}_2\text{H}_3\text{Ph}$, is obtained when a 10 per cent. alcoholic solution of phenylhydrazine is gradually added to a 10 per cent. alcoholic solution of zinc nitrate; the precipitate formed contains zinc oxide, from which it may be freed by boiling with alcohol and allowing it to crystallise. In appearance it resembles boric acid, is soluble in hot water or alcohol, but insoluble in ether or chloroform, and melts and decomposes at 170° .

The *cadmium salt*, $\text{Cd}(\text{NO}_3)_2 \cdot 3\text{N}_2\text{H}_3\text{Ph}$, may be obtained in a similar manner by using a 5 per cent. alcoholic solution of cadmium nitrate. It melts at 185° and decomposes at about 190° . The *nickel derivative*, $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$, obtained by quickly adding phenylhydrazine to a 20 per cent. alcoholic solution of nickel nitrate, forms a clear blue precipitate, which is sparingly soluble in chloroform, but insoluble in ether, and deflagrates at 141° .
J. J. S.

Action of Halogen-substituted Derivatives [of Aliphatic Compounds on Phenylhydrazine.] By HEINRICH BRUNNER and KARL EIERMANN (*Ber.*, 1898, 31, 1406—1416. Compare this vol., i, 158).—The action of chloroform on phenylhydrazine gives rise to phenylhydrazine hydrochloride, phenylic isocyanide, benzene, ammonium chloride, hydrogen chloride, and nitrogen; the same products, substituting aniline for benzene, are obtained when a solution of carbon hexachloride in ether is mixed with phenylhydrazine. Carbon tetrachloride yields phenylhydrazine hydrochloride, phenylic isocyanide, hydrogen chloride, aniline, and nitrogen; whilst ethylenic dichloride also gives rise to phenylhydrazine hydrochloride when mixed with the base. Bromoform and phenylhydrazine give the hydrobromide, along with phenylic isocyanide, benzene, hydrogen bromide, ammonium bromide, and nitrogen, the analogous change taking place under the influence of iodoform; ethylenic dibromide produces phenylhydrazine hydrobromide when mixed with the base. When chloral, diluted with 25 volumes of ether, is mixed with phenylhydrazine, nitrogen is liberated, and the hydrochloride of the base produced; the other products of the action are benzoic chloride, phenylic isocyanide, aniline, ammonia, and ammonium chloride (compare also Causse, *Abstr.*, 1897, i, 543).

The *compound*, $\text{C}_{28}\text{H}_{26}\text{N}_7\text{O}_2\text{Cl}$, obtained on mixing aqueous solutions of phenylhydrazine hydrochloride and chloral hydrate, is a reddish-brown, amorphous substance, readily soluble in alcohol, chloroform, and glacial acetic acid, but dissolving with difficulty in benzene and petroleum; it is insoluble in water and ether. The latter agent precipitates it from the solution in chloroform as a yellowish-red substance, and when separated from alcohol or glacial acetic acid by addition of feebly acidified water it is orange-coloured. It becomes brown at 140° , and chars at 145° . Nitric acid converts it into picric acid, whilst alcoholic potash eliminates ammonia, the odour of isocyanide becoming afterwards perceptible; when heated with zinc dust, it yields ammonia, aniline, and an isocyanide. The *acetyl*, *benzoyl* (two), *silver*, *ethyl*, and *propyl* derivatives are amorphous; an amorphous compound, $\text{C}_{28}\text{H}_{24}\text{N}_7\text{Cl}_3$, is obtained by the action of phosphorus pentachloride.

The *compound*, $C_{28}H_{26}N_7O_2Br$, prepared from phenylhydrazine hydrochloride and bromal hydrate, is a yellow, amorphous powder, resembling the foregoing compound in chemical behaviour. The *acetyl*, *benzoyl*, *silver*, *ethyl*, and *propyl* derivatives, and the *compound* obtained by the action of phosphorus pentachloride, are amorphous.

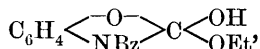
The *compound*, $C_{16}H_{16}N_3ClO$, is produced when aqueous solutions of phenylhydrazine hydrochloride and butylchloral hydrate are gently heated; the substance itself, the *acetyl*, *benzoyl*, *silver*, *ethyl*, and *propyl* derivatives, and the *compound* obtained by the action of phosphorus pentachloride, are all amorphous.

The authors discuss the possible constitution of the above-mentioned compounds. M. O. F.

Hydrocinnamide. By MARCEL DELÉPINE (*Compt. rend.*, 1898, 126, 648—651).—Hydrocinnamide, obtained by the action of ammonia on cinnamaldehyde and melting at $106-108^\circ$, is really a hydrate, $2C_{27}H_{24}N_2 + H_2O$, which explains the formation of the hydrochloride and the regeneration of the base from it by the action of ammonia. Hydrocinnamide is therefore analogous in this respect to amarine and anisine. Direct estimation of the water was found to be impracticable owing to the rapid alteration of the compound when heated.

The heat of combustion of hydrocinnamide is 8962.8 cal.; molecular heat of combustion at constant volume, 3450.68 cal.; at constant pressure, 3453.5 cal.; heat of formation -81.2 Cal.; heat of formation of the hydrate (liquid water) -79.4 Cal. It follows that $3C_9H_8O$ liquid $+ 2NH_3$ diss. $= C_{27}H_{24}N_2$ solid $+ 3H_2O$ liquid develops $+48.4$ Cal. These results show that hydrocinnamide is one of the glyoxalidines, a conclusion which is confirmed by the formation of salts, its basic function being more active than that of amarine; it may therefore be termed cinnamine. It also forms a compound with silver nitrate, and resembles amarine in its behaviour with methylic iodide and benzylic chloride. C. H. B.

The Reduction of Ethylic Orthonitrophenylic Carbonate: Ethylic Orthohydroxyphenylcarbamate. By JAMES H. RANSOM (*Ber.*, 1898, 31, 1055—1066).—Bender's ethylic amidophenylic carbonate, $NH_2 \cdot C_6H_4 \cdot O \cdot COOEt$, melting at 95° (*Abstr.*, 1887, 38), was prepared by reducing ethylic orthonitrophenylic carbonate by shaking it with tin and strong hydrochloric acid and cooling meanwhile. It is identical with Groenvik's ethylic hydroxyphenylcarbamate, $OH \cdot C_6H_4 \cdot NH \cdot COOEt$, melting at 85° (this *Journal*, 1877, i, 472), prepared from orthamidophenol and ethylic chloroformate. The true melting point of the substance is 85° ; its constitution is probably $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown NH \end{smallmatrix} \begin{smallmatrix} \diagup C \\ \diagdown \end{smallmatrix} \begin{smallmatrix} \diagup OH \\ \diagdown OEt \end{smallmatrix}$. It yields a *benzoyl* derivative,



which melts at 75.5° ; this can also be obtained from ethylic chloroformate and benzoylorthamidophenol, $OH \cdot C_6H_4 \cdot NHBz$, which is itself best obtained by the action of benzoic chloride (1 mol.) on orthamidophenol (2 mols.) in ethereal solution. When this benzoyl derivative is heated in a bath at $240-245^\circ$, alcohol comes over first, then a

small quantity of ethylic benzoate, and, lastly, a fraction which contains *benzoylcarbonylamidophenol*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{O} \\ \text{NBz} \end{smallmatrix}\rangle\text{CO}$, melting at $173\text{--}174^\circ$, together with a little carbonylamidophenol (from which the former can be prepared by benzylation), and a little *benzenylamidophenol*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{O} \\ \text{N} \end{smallmatrix}\rangle\text{CPh}$, which melts at $101\text{--}102^\circ$, and can also be prepared by distilling benzoylcarbonylamidophenol.

Orthanisidine, when heated with ethylic chloroformate in alkaline aqueous solution, yields *ethylic orthomethoxyphenylcarbamate*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COOEt}$, boiling at $180\text{--}182^\circ$ under 26 mm. pressure. A product identical with this ought to be obtained by methylating the original substance mentioned above, if Groenvik's formula for it were correct; this substance could not be made to yield a methylic derivative, however. Ethylic orthomethoxyphenylcarbamate, when treated with bromine in carbon bisulphide solution, yields a *monobromo*-substitution derivative which melts at $101\cdot5\text{--}102\cdot5^\circ$.

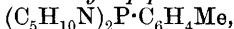
Ethylic paranitrophenylic carbonate can be prepared from paranitrophenol in alkaline solution by the action of ethylic chloroformate, and also by dissolving ethylic phenylic carbonate in fuming nitric acid at 0° ; it melts at $67\text{--}68^\circ$. Unlike the ortho-isomeride, it is reduced by tin and alcoholic hydrochloric acid, in the normal manner, to *ethylic paramidophenylic carbonate*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{COOEt}$, which melts at $35\text{--}36^\circ$; the *hydrochloride* of this melts and decomposes at 197° , the yellow *platinochloride* melts at 237° , and the *carbamide* (from the hydrochloride and potassium cyanate) at $149\text{--}150^\circ$. C. F. B.

Some-N-Phosphines and N-Phosphonium Compounds. By C. A. AUGUST MICHAELIS (*Ber.*, 1898, 31, 1037—1047).—Compounds analogous to those prepared from phosphorus trichloride and piperidine (*Abstr.*, 1895, i, 682) have been prepared with phosphenyl chloride, PPhCl_2 , and similarly constituted chlorides, instead of phosphorus chloride. These trichlorides react with tetrahydroquinoline also, but the reaction is less energetic, and there is no need to cool with ice, or even to dilute with ether; the products, too, form phosphonium compounds less readily than the analogous piperidine derivatives, and that only with methylic iodide, as a rule. No aliphatic N-phosphines have been obtained as yet.

[With GEORG SCHLÜTER].—*Phenyldipiperidine-N-phosphine*, $(\text{C}_5\text{H}_{10}\text{N})_2\text{PPh}$, from piperidine (4 mols.) and phosphenyl chloride (1 mol.) in ethereal solution, melts at 78° . With chlorine gas in light petroleum solution, it yields deliquescent *phenyldipiperidine-N-phosphine chloride*, $(\text{C}_5\text{H}_{10}\text{N})_2\text{PPhCl}_2$; this is converted by water into the *phosphine oxide*, $(\text{C}_5\text{H}_{10}\text{N})_2\text{PPhO}$, which is better prepared, however, by the action of phosphenyl oxychloride, PPhOCl_2 , on piperidine; it is hygroscopic and melts at 68° . The *phosphine sulphide*, obtained by prolonged heating of the phosphine with excess of sulphur at 130° , melts at 92° and is very stable. With carbon bisulphide, the phosphine first forms a yellowish-white compound, probably $(\text{C}_5\text{H}_{10}\text{N}\cdot\text{CS}\cdot\text{S})_2\text{PPh}$, which melts at 144° ; when

crystallised repeatedly from a mixture of benzene with ether, this loses half its carbon bisulphide, yielding a yellow substance, presumably $C_5H_{10}N \cdot CS \cdot S \cdot PPh \cdot NC_5H_{10}$, which melts at 137° . *Phenyldipiperidinemethylphosphonium iodide* (from the phosphine and methylic iodide at the ordinary temperature), *chloride*, and yellowish-red *platinochloride*, $(C_5H_{10}N)_2PPhMeI$, &c., melt at 167° , 130° , and 178° respectively; the *ethylphosphonium iodide* at 174° , and the yellow, deliquescent *benzylphosphonium chloride* at 204° . The methylphosphonium hydroxide is a syrup; when heated, it loses piperidine and forms methylphenylphosphinic acid, $O \cdot PPhMe \cdot OH$.

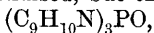
[With FREUNDLICH.]—*Paratolyldipiperidine-N-phosphine*,



melts at 80° ; the hygroscopic *phosphine oxide*, $(C_5H_{10}N)_2PO \cdot C_6H_4Me$, at 60° ; the *phosphine sulphide* at 88° , and the pale yellow compound with carbon bisulphide (2 mols., a compound with $1CS_2$ could not be obtained) at 139° . The *methyl-, ethyl-, propyl- and isobutyl-phosphonium iodides*, $(C_5H_{10}N)_2P \cdot C_6H_4Me, MeI$, &c., melt at 186° , 191° , 197° , and 204° respectively; the *benzylphosphonium chloride* at 125° . By heating the methylphosphonium hydroxide at 150 — 180° , *paratolylmethylphosphinic acid*, $C_6H_4Me \cdot PMeO \cdot OH$, was obtained; it melts at 120° ; its *silver salt* was analysed.

[With CURT ROEBER.]—*Chlorophenyl-, anisyl-, and phenetyl-dipiperidine-N-phosphines*, $(C_5H_{10}N)_2P \cdot C_6H_4R$ [$R = Cl$; OMe ; OEt], melt at 95° , 69° and 84° respectively. They were prepared in the same way as phenyldipiperidine-*n*-phosphine, and resemble that substance in their reactions.

[With J. GROSSHEIM.]—*Tetrahydroquinoline-N-phosphine*, $(C_9H_{10}N)_3P$, from tetrahydroquinoline and phosphorous chloride, melts at 202 — 204° , and is decomposed by acids into tetrahydroquinoline and phosphorous acid; it cannot readily be oxidised, but the *phosphine oxide*,



is obtained by the action of tetrahydroquinoline on phosphorus oxychloride; it melts at 90 — 91° . The N-phosphine (1 mol.) will unite with sulphur (1 mol.), however, at 170° , but not very readily; the resulting *phosphine sulphide*, $(C_9H_{10}N)_3PS$, crystallises in the regular system and melts at 192° . *Tetrahydroquinolinemethylphosphonium iodide, chloride*, and reddish-yellow *platinochloride*, $(C_9H_{10}N)_3PMeI$, &c., melt at 188° , 148 — 150° , and 230° respectively.

Phenylditetrahydroquinoline-N-phosphine, $(C_5H_{10}N)_2PPh$, from tetrahydroquinoline and phosphenyl chloride, melts at 150° ; the *phosphine oxide*, $(C_5H_{10}N)_2PPhO$, at 216° , and the *methylphosphonium iodide*, $(C_5H_{10}N)_2PPhMeI$, at 136° .

Paratolylditetrahydroquinoline-N-phosphine, $(C_5H_{10}N)_2P \cdot C_6H_4Me$, melts at 140° , the *phosphine oxide*, $(C_5H_{10}N)_2PO \cdot C_6H_4Me$, at 181° .

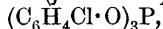
C. F. B.

Behaviour of Alkylid Iodides with Alkylid Phosphites, or O-Phosphines. By C. A. AUGUST MICHAELIS and R. KAEHNE (*Ber.*, 1898, 31, 1048—1055).—The phenylic, parachlorophenylic, para- and meta-tolylic, and pseudocumenylic salts of phosphorous acid, $(OR_3)_3P$

(1 mol.), react with methylic iodide (1 mol.) at suitable temperatures, and also with benzylic chloride, yielding compounds, $(\text{OR})_3\text{PMeI}$ or $(\text{OR})_3\text{PCl}\cdot\text{CH}_2\text{Ph}$; with ethylic iodide, they would not combine in the same way; the products were often oils, but these sometimes solidified on cooling, or on washing with ether. They are decomposed by alkalis, and even by water, hydriodic acid, phenol, and an alkylic methyl- or benzyl-phosphinate being formed, $(\text{OR})_3\text{PMeI} + \text{H}\cdot\text{OH} = \text{HI} + \text{R}\cdot\text{OH} + (\text{OR})_2\text{PMeO}$. Ethylic phosphite will not combine with methylic iodide; instead of a normal compound, its decomposition products are obtained; one of these is *methylphosphinic acid*, for the preparation of which this reaction is convenient (see later.)

Triphenolmethyl-O-phosphonium iodide, $(\text{OPh})_3\text{PMeI}$, prepared as indicated at 100° , melts at $70\text{--}75^\circ$, and is very deliquescent; *phenylic methylphosphinate*, $(\text{OPh})_2\text{PMeO}$, melts at $36\text{--}37^\circ$. *Triphenolbenzyl-O-phosphonium chloride*, $(\text{OPh})_3\text{PCl}\cdot\text{CH}_2\text{Ph}$, prepared at 175° , was not obtained pure; *phenylic benzylphosphinate*, $(\text{OPh})_2\text{PO}\cdot\text{CH}_2\text{Ph}$, melts at 60° .

Parachlorophenylic phosphite (parachlorophenol-O-phosphine),



boils at $290\text{--}297^\circ$ under 15 mm. pressure. *Triparachlorophenolmethyl-phosphonium iodide*, $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{O})_3\text{PMeI}$, melts at 71° . *Parachlorophenylic methylphosphinate*, $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{O})_2\text{PMeO}$, boils at about 245° under 20 mm. pressure.

Paratolylic phosphite (triparacresol-O-phosphine), $(\text{C}_6\text{H}_4\text{Me}\cdot\text{O})_3\text{P}$, from paracresol (3 mols.) and phosphorous chloride (1 mol.), boils at $250\text{--}255^\circ$ under 10 mm. pressure. *Triparacresolmethyl-O-phosphonium iodide*, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{O})_3\text{PMeI}$, prepared at 100° , could not be obtained quite pure; *paratolylic methylphosphinate*, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{O})_2\text{PMeO}$, boils at $220\text{--}225^\circ$ under 12 mm. pressure.

Metatolylic phosphite (trimetacresol-O-phosphine) boils at $235\text{--}238^\circ$ under 7 mm. pressure, at $240\text{--}243$ under 10 mm. *Trimetacresolmethyl-O-phosphonium iodide*, prepared at 100° , is very hygroscopic, and was not obtained pure; *metatoluic methylphosphinate* boils at $200\text{--}205^\circ$ under 7 mm. pressure.

Pseudocumenylic phosphite (pseudocumenol-O-phosphine),



boils at $270\text{--}274^\circ$ under 16 mm. pressure, and has a sp. gr. = 1.097 at 17° . The methylphosphonium iodide was not obtained solid. *Pseudocumenylic methylphosphinate*, $(\text{C}_6\text{H}_2\text{Me}_3\cdot\text{O})_2\text{PMeO}$, melts at $79\text{--}90^\circ$.

When ethylic phosphite is heated with methylic iodide for 12 hours at 220° , an inflammable gas, presumably ethylene, is formed, and also ethylic iodide, and a solid product from which methylphosphinic acid, $\text{PMeO}(\text{OH})_2$, can be isolated. This solid is dissolved in nitric acid, fuming nitric acid added, and the whole evaporated to dryness; the residue is then dissolved in water, and treated with excess of lead oxide made into a thin paste with water. From the mixture of lead salts formed, lead oxide and lead methylphosphinate are extracted with excess of acetic acid, lead phosphate remaining undissolved, the lead

in the filtrate is precipitated with hydrogen sulphide, and the filtrate freed from acetic acid by repeated evaporation with water, when the methylphosphinic acid is left as a white, crystalline mass, resembling spermaceti in appearance.

C. F. B.

Action of Phosphorus Thiochloride on Solutions of Phenols in Aqueous Alkalis. By WILHELM AUTENRIETH and OTTO HILDEBRAND (*Ber.*, 1898, 31, 1094—1111. Compare this vol., i, 14).—When a solution of phenol in 15—20 per cent. aqueous soda is heated on the water bath with phosphoryl thiochloride, *triphenylic thiophosphate*, PS(OPh)_3 , is formed and crystallises from alcohol in slender prisms melting at 53° . It is scarcely attacked by aqueous alkalis, but is readily hydrolysed by alcoholic soda, *diphenoxythiophosphoric acid*, $\text{PS(OPh)}_2\cdot\text{OH}$, being produced. This substance is, moreover, always formed by the action of the thiochloride on an alkaline solution of phenol, both in the cold and on heating, and is also produced by the hydrolysis of diphenoxythiophosphoryl chloride with alcoholic soda; it is a yellowish oil which cannot be distilled, and readily dissolves in alkalis. The *sodium* salt crystallises in lustrous plates and is soluble in alcohol.

When phosphoryl thiochloride is added to a well cooled alkaline solution of phenol, two compounds are produced, which are the mono- and di-phenoxy-derivatives. *Diphenoxythiophosphoryl chloride*, $\text{PS(OPh)}_2\text{Cl}$, crystallises in forms resembling those of gypsum, and melts at $66\text{--}67^\circ$; it is stable towards water, hydrochloric acid, and aqueous alkalis, but is converted by alcoholic soda into diphenylthiophosphoric acid. The chloride is converted by aqueous ammonia into *diphenoxythiophosphamide*, $\text{PS(OPh)}_2\cdot\text{NH}_2$, which crystallises in white, nacreous plates melting at 115° , and is sparingly soluble in hot water. *Diphenoxythiophosphanilide*, $\text{PS(OPh)}_2\cdot\text{NHPh}$, formed by the action of aniline on the amide, crystallises in slender prisms melting at 92° . *Diphenoxythiophosphodiethylamide*, $\text{PS(OPh)}_2\cdot\text{NEt}_2$, crystallises in lustrous prisms melting at 58° .

Phenoxythiophosphoryl dichloride, $\text{OPh}\cdot\text{PSCl}_2$, is a colourless liquid which can be distilled under diminished pressure. *Phenoxythiophosphodiamide*, $\text{PS(OPh)(NH}_2)_2$, crystallises in lustrous plates melting at 119° ; *Phenoxythiophosphodianilide*, $\text{OPh}\cdot\text{PS(NHPh)}_2$, forms lustrous crystals melting at 126° , whilst the corresponding *phenylhydrazide*, $(\text{OPh})\cdot\text{PS(NH}\cdot\text{NHPh)}_2$, crystallises in lustrous, slender needles melting at 136° .

Phenoxythiophosphamic acid, $\text{OPh}\cdot\text{PS(NH}_2)\cdot\text{OH}$, is prepared by heating the dichloride with aqueous ammonia, and crystallises in slender needles melting at $127\text{--}128^\circ$; when boiled with water, it yields ammonium phosphate, phenol and hydrogen sulphide. Alcoholic soda converts the dichloride into *phenoxythiophosphoric acid*, $\text{OPh}\cdot\text{PS(OH)}_2$, which has only been obtained as a syrup.

Paracresol readily reacts with phosphorus thiochloride, but the sole product of the reaction appears to be *diparatolyloxythiophosphoryl chloride*, $\text{PS(O}\cdot\text{C}_6\text{H}_4\text{Me)}_2\text{Cl}$, which melts at 53° , and closely resembles the corresponding phenyl derivative in its properties. *Diparatolyloxy-*

thiophosphamide, $\text{PS}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_2\cdot\text{NH}_2$, crystallises in lustrous plates melting at 131° , whilst the *anilide* crystallises in slender needles and melts at 106° .

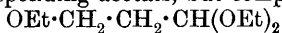
Triparachlorophenylic thiophosphate, $\text{PS}(\text{O}\cdot\text{C}_6\text{H}_4\text{Cl})_3$, crystallises in tablets and melts at 113 — 114° . *Diparachlorophenoxythiophosphoryl chloride*, $\text{PS}(\text{O}\cdot\text{C}_6\text{H}_4\text{Cl})_2\text{Cl}$, melts at 92° , and when treated with ammonia yields the corresponding *amide*, which crystallises in lustrous plates melting at 96° .

β -Naphthol reacts very vigorously with the thiochloride, forming a mixture of the mono- and di-chlorides, which cannot be directly separated, but when treated with ammonia yields the corresponding amides, which can readily be obtained pure. *β -Naphthoxythiophosphodiamide*, $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{PS}(\text{NH}_2)_2$, crystallises in lustrous plates melting at 176° , whilst *β -naphthoxythiophosphamide*, $\text{PS}(\text{OC}_{10}\text{H}_7)_2\cdot\text{NH}_2$, separates from dilute alcohol in slender needles melting at 215° . A. H.

Iodinium Compounds Prepared by the Action of the Iodo-chlorides on Mercury Organic Compounds. By CONRAD WILLGERODT (*Ber.*, 1898, 31, 915—922).—The iodochlorides react with mercurydiphenyl and phenylmercuric chloride to form double salts of the iodinium chlorides with mercuric chloride. *Diphenyliodinium mercurichloride*, $(\text{Ph}_2\text{ICl})_2\cdot\text{HgCl}_2$, which decomposes at 203° , is formed by the action of phenyliodochloride both on mercurydiphenyl and phenylmercuric chloride, and is also produced when solutions of diphenyliodinium chloride and mercuric chloride are mixed. Phenylmercuric chloride does not appear to form any similar double salt, and the author was unable to obtain the salt, $\text{Ph}_2\text{ICl}\cdot\text{HgCl}_2$, described by Hartmann and Meyer (*Abstr.*, 1894, i, 461). *Phenylorthotolyiodinium chloride*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{IPhCl}$, crystallises in short prisms melting at 213 — 214° ; the *platinochloride* in yellow needles, decomposing at about 191° ; the *mercurichloride* in long, white needles melting at 135 — 137° , whilst the *dichromate* decomposes at 141 — 143° ; the *iodide* crystallises in short, colourless prisms decomposing at 165° ; the *nitrate* decomposes at 183 — 185° , and the *sulphate* at 171° . The corresponding *hydroxide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{IPh}\cdot\text{OH}$, has hitherto only been obtained in aqueous solution. *Phenylparatolyiodinium chloride* forms large, white prisms, melts at 208° , and is more readily soluble in water than the ortho-compound. The *platinochloride* decomposes at 195 — 198° ; the *dichromate* explodes at 155 — 157° and the *iodide* decomposes at 170° , whilst the *mercurichloride* crystallises in matted plates, melting at 157° , and the *nitrate* in large plates melting at 138 — 140° . The hydroxide has only been obtained in the form of an amorphous, varnish-like mass. *Phenyl- β -naphthyl iodinium chloride*, $\text{C}_{10}\text{H}_7\cdot\text{IPhCl}$, crystallises in short, acicular plates melting at 197° , and forms a *platinochloride* which decomposes at 171 — 173° , and an *iodide* which decomposes at 156 — 160° . The *hydroxide* forms a crystalline mass which has a strongly alkaline reaction. It was found impossible to obtain a phenylethyl iodinium chloride by the action of an iodochloride on either mercury ethide or ethylmercurichloride, the products being ethylic chloride, iodobenzene, and ethylmercurichloride or mercuric chloride. A. H.

Acetals of Aldehydes and Ketones. By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1010—1019. Compare E. Fischer and Giebe, this vol., i, 168).—Pursuing his discoveries regarding the formation of acetals of aldehydes, ketones, and ketonic acids by the agency of orthoformates (Abstr., 1896, i, 464; 1897, i, 188), the author has been led to replace the orthoformates by the hydrochlorides of imidoformates; these are known to yield orthoformates with alcohol at the ordinary temperature (Pinner, Abstr., 1883, 731), and they are now found to react with ketones, &c., in alcoholic solution, yielding acetals in accordance with the equation $\text{CR}_2\text{O} + 2\text{EtOH} + \text{OEt}\cdot\text{CH}\cdot\text{NH}\cdot\text{HCl} = \text{CR}_2(\text{OEt})_2 + \text{H}\cdot\text{COOEt} + \text{NH}_4\text{Cl}$. The ketone (1 mol.) is mixed with alcohol (5 mols.), the mixture well cooled, and the imidoformate hydrochloride ($1\frac{1}{4}$ mols.) is gradually added, after which the whole is allowed to remain for several days, first in a refrigerator, then at the ordinary temperature. Plenty of ether is then added, the liquid is filtered from ammonium chloride, treated with ice and water containing a few drops of ammonia, and the ethereal layer removed and dried with potassium carbonate. The ether is next evaporated, and the residue fractionated under diminished pressure if the acetal have a high boiling point, otherwise under atmospheric pressure, in which case it is advisable first to let the liquid remain for some time with plenty of calcium chloride, in order that the alcohol may be removed as completely as possible. In some cases, no reaction occurs; for example, with benzophenone, although acetophenone does react, ethylic benzoylformate yields no acetal, although the pyruvate (acetylformate) does. Nor does camphor or carvole yield an acetal; the latter, in fact, gives + limonene. The yield is about the same as by E. Fischer's method in the case of aliphatic and of nitro- and chloro-aromatic aldehydes; those aldehydes which correspond with stronger acids seem to give a larger yield. In the case of other aromatic aldehydes, the new method is to be preferred, and it also yields acetals in the case of ketones, unlike the other method. By using methylic alcohol and methylic imidoformate, dimethylacetals can be obtained. The acetals obtained are enumerated below, together with such of their constants (boiling points and specific gravities at 15°) as have not been published before; when the name of the aldehyde, &c., is alone given, the *ethyl*-acetal only is described in the paper.

Acetaldehyde, cœnanthaldehyde, acraldehyde, and crotonaldehyde do not yield the corresponding acetals, but compounds



and $\text{OEt}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, the latter of which boils at $73\text{--}74^\circ$ under 14 mm. pressure. [The author prefers these formulæ to those, $\text{OEt}\cdot\text{CHMe}\cdot\text{CH}(\text{OEt})_2$ and $\text{OEt}\cdot\text{CHEt}\cdot\text{CH}(\text{OEt})_2$, proposed by Newbury (Abstr., 1891, 285)]. *αβ-Dibromopropaldehyde*: dimethylacetal, 108° , under 15 mm.; diethylacetal, $127\text{--}129^\circ$, under 22 mm.; the latter of these is converted by alcoholic potash into the diethylacetals of *monobromacraldehyde*, $181\text{--}183^\circ$, and *propiolaldehyde*, 140° . Furfuraldehyde: diethylacetal, $189\text{--}191^\circ$, sp. gr. = 1.0075. Benzaldehyde. *Cuminaldehyde*: dimethylacetal, $244\text{--}245^\circ$, sp. gr. = 1.0633; diethylacetal, $257\text{--}259^\circ$, sp. gr. = 0.9254. *Metanitrobenzaldehyde*: dimethylacetal, $162\text{--}164^\circ$ under 19 mm., sp. gr. = 1.209; diethylacetal, 178° , under 21 mm., sp. gr. = 1.131. *Anisaldehyde*: dimethylacetal; diethylacetal, $261\text{--}263^\circ$; sp.

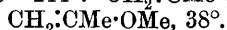
gr. = 0.9908. *Piperonaldehyde*: dimethylacetal, sp. gr. = 1.206; *diethylacetal*, 279—281° (153—154°, under 11 mm.), sp. gr. 1.129. *Cinnamaldehyde*; *dimethylacetal*, 125—127°, under 11 mm., sp. gr. = 1.023; *diethylacetal*, 264—266° (140—142°, under 12 mm.), sp. gr. = 0.981. *Monobromocinnamaldehyde*: *dimethylacetal*, 161—162°, under 15 mm., sp. gr. = 1.358; *diethylacetal*, 170—171°, under 15 mm., sp. gr. = 1.266; both of these yield acetals of *phenylpropionaldehyde* when heated with alcoholic potash.

Acetone. *Acetophenone*: *dimethyl*-, *diethyl*- (212—216°, with some decomposition; compare following abstract), and *dipropyl*-acetals. *Ethyl pyruvate*: *diethylacetal*, 190—191°. [A fuller account of the acetals of ketones and ketonic acids is to be given in a later paper.]

Acetaldehyde diethylacetal (1 mol.), when heated with acetic anhydride (1 mol.) at 150° in a sealed tube, yields a compound, $\text{OAc} \cdot \text{CHMe} \cdot \text{OEt}$, boiling at 125—130°; sp. gr. = 0.941. In a similar way (except that further heating at 200° is necessary), benzaldehyde diethylacetal yields a compound $\text{OAc} \cdot \text{CHPh} \cdot \text{OEt}$, boiling at 243—245°. C. F. B.

Action of Agents which can remove the elements of Alcohol on some Acetals. By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1019—1021).—In the case of ethylic acetoacetate diethylacetal (*Abstr.*, 1896, 464), it has been shown that distillation under atmospheric pressure can remove the elements of alcohol from an acetal, $\text{CH}_3 \cdot \text{CR}(\text{OEt})_2$, forming a compound $\text{CH}_2 \cdot \text{CR}(\text{OEt})$. In general, however, this is not the case; some agent is necessary in order to remove the alcohol. Phosphoric anhydride may be used (as with ethylic pyruvate acetal), but it cannot be used alone in the case of acetals of aldehydes and ketones, for these, especially the latter, are very easily decomposed by acids. A mixture of phosphoric acid with a tertiary amine, such as pyridine or quinoline (ordinary acetal), may be used however; the base serves to neutralise the ethylphosphoric acid which is formed. In the case of acetals that more readily lose alcohol, the phosphoric anhydride may be replaced by an acid chloride; if the expected product have a low boiling point, quinoline and benzoic chloride should be used; if a high one, pyridine and acetic chloride (acetophenone acetal). A few compounds prepared by this method from acetals are enumerated below, with their boiling points; a more detailed account is to be published later.

Ethyl α -ethoxyacrylate, $\text{CH}_2 \cdot \text{C}(\text{OEt}) \cdot \text{COOEt}$, 180°; hydrolysis converts it into *α -ethoxyacrylic acid*, which melts at 62°. [Merz and Otto's acid, melting at 110° (*Abstr.*, 1890, 957), is possibly the β -ethoxy acid]. $\text{CH}_2 \cdot \text{CPh} \cdot \text{OEt}$, 209—211°. $\text{CH}_2 \cdot \text{CMe} \cdot \text{OEt}$, 59—62°;



Ethyl vinyl ether, $\text{CH}_2 \cdot \text{CH} \cdot \text{OEt}$.

C. F. B.

Propargylaldehyde [*Propiolaldehyde*] and Phenylpropargylaldehyde [*Phenylpropionaldehyde*]. By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1021—1023).—The acetals of these aldehydes are prepared by heating the acetals of $\alpha\beta$ -dibromopropionaldehyde and α -bromocinnamaldehyde respectively with alcoholic potash; when heated with dilute sulphuric acid, they yield the aldehydes. These aldehydes are decomposed by aqueous soda in the cold, acetylene or phenylacetylene

being evolved and a formate formed; the action is in some respects analogous to that of alkalis on chloral.

Propiolaldehyde, $\text{CH}_2\text{C}\cdot\text{CHO}$, boils at $59-61^\circ$, and affects the nose and eyes even more than acetaldehyde does. A crystalline anilide and hydrazone were prepared. The *dimethylacetal* boils at 110° , the *diethylacetal* at $139-141^\circ$; the latter forms a feebly explosive silver derivative, $\text{C}_2\text{Ag}:\text{C}\cdot\text{CH}(\text{OEt})_2$.

Phenylpropiolaldehyde, $\text{C}_6\text{H}_5\text{C}\cdot\text{CHO}$, which boils at 118° under 17 mm. pressure, decomposes and gives off carbonic oxide when distilled under atmospheric pressure. The anilide, hydrazone, phenylhydrazone, semicarbazone, and hydrocyanide were prepared, and also condensation products with acetone, acetophenone, and malonic acid. The *diethylacetal* boils at 148° under 14 mm. pressure.

C. F. B.

Normal Octyl Compounds. By PAUL LIPINSKI (*Ber.*, 1898, 31, 938—942).—*Octylphenyl methyl ketone*, $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$, formed by the action of acetic chloride on octylbenzene in the presence of aluminium chloride, is a yellowish oil with a faint aromatic odour. The *oxime* crystallises in white plates melting at $42-43^\circ$. *Octylphenyl phenyl ketone*, $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$, is a yellowish-brown oil which boils at $104-110^\circ$ under a pressure of 85 mm., and yields an *oxime* melting at $106-107^\circ$. *Octylphenylazo- α -naphthol*, $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, crystallises from alcohol in red plates, which are prepared by nitrating octylbenzene, reducing, and treating the solution of the product of reduction with nitrous acid and α -naphthol. *Paramethyloctylbenzene* (para-octyltoluene) melts at $11-12^\circ$, boils at $281-283^\circ$, and is converted by oxidation into terephthalic acid. *Para-octyltoluenesulphonic* [*paramethyloctylsulphonic*] acid, obtained by shaking paramethyloctylbenzene with fuming sulphuric acid, forms white, deliquescent crystals. The salts of *barium* and *lead* are soluble in water and crystallise well. *Mononitroparamethyloctylbenzene*, $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$, which is produced, along with the dinitro-compound, by the action of fuming nitric acid on paramethyloctylbenzene, melts at $19-20^\circ$, forming a yellowish oil which cannot be distilled. The *dinitro*-compound is also an oil which cannot be distilled. *Paramethyloctylphenyl methyl ketone*, $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$, is a yellowish liquid which has not been further examined.

A. H.

A New Method of Preparing Acid Cyanides. By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1023—1024).—When pyridine is added slowly to an ethereal solution of benzoic chloride and anhydrous hydrogen cyanide, benzoic cyanide is obtained, together with some dibenzoic dicyanide: $\text{C}_6\text{H}_5\cdot\text{COCl} + \text{HCN} + \text{C}_5\text{NH}_5 = \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CN} + \text{C}_5\text{NH}_5\cdot\text{HCl}$. The reaction is probably a general one, and affords a convenient means of preparing acid cyanides. If the acid chloride be added to a mixture of hydrogen cyanide with pyridine, the polymeric cyanide is almost the only product.

C. F. B.

Paraxylylacetic Acid. By GUERBET (*Compt. rend.*, 1897, 125, 34—37).—A good yield of Claus' paraxylyl methyl ketone can only be obtained under the following conditions. Aluminium chloride (20 grams), placed in a reflux apparatus, is covered with dry

carbon bisulphide, the flask is heated to 50° , and a mixture of acetic chloride (75 grams) and paraxylene (100 grams) gradually added from a dropping funnel, a further quantity of aluminium chloride (40 grams) being finally added. The operation takes about half an hour, and the mixture is then poured on to ice.

Paraxylylacetamide, obtained when the ketone (5 grams), 95 per cent. alcohol (4 grams), ammonium hydrosulphide (15 grams), and sulphur (2 grams) are heated for 48 hours at 200° , crystallises from alcohol in large, colourless needles melting at 154° . When hydrolysed by boiling with alcoholic potash (33 per cent.) for 8 days, it yields *paraxylylacetic acid*, $C_6H_3Me_2 \cdot CH_2 \cdot COOH$, which crystallises from 60 per cent. alcohol in colourless, prismatic needles melting at 128° . The *potassium* salt is extremely deliquescent; the *sodium* salt crystallises with $1H_2O$, the *calcium* salt with $3H_2O$; the *barium* salt is anhydrous and much more soluble than the calcium salt. The *methylic* salt boils at $253-254^{\circ}$, and the *ethylic* salt at 261.5° .

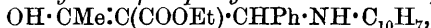
When oxidised with potassium permanganate, the acid yields unsymmetrical trimesic acid. J. J. S.

Tautomerides. By ROBERT SCHIFF (*Ber.*, 1898, 31, 1388—1395. Compare this vol., i, 237).—The author has shown that sodium ethoxide converts the ketonic modification of ethylic benzylidenedi-acetoacetate into the enolic form, which develops an intense coloration with ferric chloride, whilst piperidine exerts the converse influence.

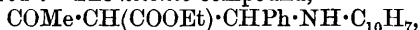
When ethylic ethylidenedi-acetoacetate (Knoevenagel, *Abstr.*, 1895, i, 51), is prepared from ethylic acetoacetate (2 mols.) and acetaldehyde (1 mol.) in presence of piperidine, the ketonic form crystallises from the liquid, and develops no coloration with ferric chloride; when the alcoholic solution is boiled, however, the enolic isomeride is generated. In order to prepare the latter, the ketonic salt is mixed with cold alcoholic sodium ethoxide (2 mols.), and, in presence of ice, treated with the corresponding amount of dilute hydrochloric acid; lustrous needles separate, developing a deep violet coloration with ferric chloride, but this property is gradually lost when the crystals are exposed to air, until, when quite dry, the substance is indifferent towards the agent, and melts at $78-79^{\circ}$.

Benzylideneaniline is a convenient agent for fixing tautomeric forms; in fact, all analogous condensation products of aromatic bases and aldehydes, excepting salicylaldehyde, appear suitable for this purpose.

Enolic ethylic benzylidene- β -naphthylamidoacetoacetate,



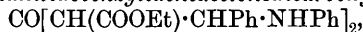
is prepared by adding finely divided benzylidene- β -naphthylamine to the enolic modification of ethylic acetoacetate (Kahlbaum); it dissolves in a small proportion of warm benzene, and separates as a white, crystalline precipitate on adding petroleum to the cold solution. It melts at $100-101^{\circ}$. The *ketonic* compound,



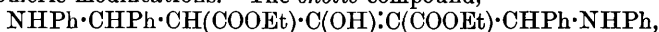
is obtained from common specimens of ethylic acetoacetate by adding benzylidene- β -naphthylamine, and a small quantity of piperidine; it

melts at 74—75°, and yields ethylic phenylcarbinolacetoacetate (*loc. cit.*) under the influence of sodium ethoxide.

Ketonic ethylic dianilidobenzylideneacetonedicarboxylate,

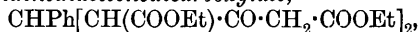


is obtained on adding a few drops of piperidine to mixed solutions of ethylic acetonedicarboxylate and benzylideneaniline (2 mols.) in benzene; it melts at 117—118°, and gives no coloration with ferric chloride. When piperidine is not employed, a mixture of the ethereal salt and benzylideneaniline (2 mols.) yields, after some hours, a white, insoluble compound which melts at 134°, and is isomeric with the foregoing substance; the authors regard it as a mixture form of the tautomeric modifications. The *enolic* compound,



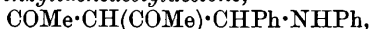
is produced on mixing benzene solutions of ethylic acetonedicarboxylate and benzylideneaniline in molecular proportion; the white, micro-crystalline substance is washed with light petroleum and benzene, and melts at 139°.

Ethylic benzylidenediacetonedicarboxylate,



prepared by adding 2 vols. of alcohol and a small quantity of piperidine to a mixture of benzaldehyde and ethylic acetonedicarboxylate (2 mols.), melts at 130°, and is in part resolved into its components under the influence of boiling alcohol.

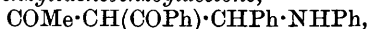
Ketonic anilidobenzylideneacetylacetone,



is obtained on adding a small quantity of piperidine to a mixture of benzylideneaniline and acetylacetone in molecular proportion; it separates when petroleum is added to its benzene solution, and melts at 83—84°. The substance develops a feeble red coloration with ethereal ferric chloride. The *compound* obtained without the influence of piperidine is the isomeric mixture form, and melts at 103°; it develops an intense red coloration with ferric chloride. The *enolic* compound, $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{COMe})\cdot\text{CHPh}\cdot\text{NHPh}$, is formed in presence of a small quantity of dry sodium ethoxide; it crystallises from benzene on the addition of petroleum, in lustrous, white needles and melts at 109°. A deep red coloration with ferric chloride reveals the hydroxylic character of this modification.

Benzylidenediacetylacetone (Knoevenagel, *loc. cit.*), resembles ethylic benzylidenediacetoacetate and ethylic ethylidenediacetoacetate in chemical behaviour; the ketonic form melts at 167—168°, and is indifferent towards ferric chloride.

Ketonic anilidobenzylidenebenzoylacetone,

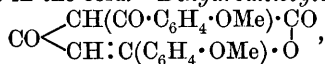


cannot be crystallised owing to its insoluble character; it melts at 172—173°, and is probably a polymeride. The *enolic* compound, $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{COPh})\cdot\text{CHPh}\cdot\text{NHPh}$, crystallises very slowly from petroleum, and melts at 83—84°; it develops an intense dark red coloration with ferric chloride.

M. O. F.

Ethylic Anisoylacetoacetate and its Derivatives. By ALBERT SCHOONJANS (*Chem. Centr.*, 1897, ii, 616; from *Bull. Acad. roy. Belg.*, [iii], 33, 810—820).—A yield of 110 per cent. of anisic chloride is

obtained from anisic acid by heating the dry acid (1 mol.) with phosphorus pentachloride (1 mol.), then removing the phosphorus oxychloride by means of a current of dry air, and distilling the residue on a L. Meyer's air bath. *Anisic chloride* is a colourless, highly refractive liquid, boils at 160—164° under a pressure of 35 mm., at 152—153° under 24 mm., and at 145° under 14 mm.; when mixed with cold water and cooled, it forms matted needles which melt at 22°. *Ethylic anisoylacetoacetate*, prepared like the benzoylacetoacetate, forms an oily liquid which decomposes when distilled in a vacuum. With copper acetate, its alcoholic solution forms the compound $\text{Cu}(\text{C}_{14}\text{H}_{15}\text{O}_5)_2$, which crystallises from hot alcohol in small tablets, and from chloroform, in which it is very soluble, in small, lustrous needles. When ethylic anisoylacetoacetate is shaken with twice its weight of 10 per cent. ammonia, a yellow precipitate forms which dissolves on warming, and then *ethylic anisoylacetate* separates as a colourless oil of pleasant odour; this oil is insoluble in water, but miscible with alcohol and ether, boils at 140—142° under a pressure of 10 mm., has a sp. gr. = 1.0338 at 19°, gives a deep red coloration with ferric chloride in alcoholic solution, and with copper acetate an olive-green substance, $\text{Cu}(\text{C}_{12}\text{H}_{13}\text{O}_4)_2$, which crystallises from alcohol or chloroform in small needles, and decomposes at 180°. By the action of hydroxylamine hydrochloride in glacial acetic acid on ethylic anisoylacetate, a substance, which is probably *anisylisoxazolone*, is formed; it crystallises from hot alcohol in long, yellow needles, melts and decomposes at 143°, is slightly soluble in light petroleum, easily soluble in hot benzene, and soluble in cold alkalis; with ferric chloride in alcoholic solution, it forms an inky-black liquid, reduces ammoniacal silver solutions, and is easily decomposed by alcoholic potassium hydroxide in the cold. *Dehydroanisoylacetic acid*,



is obtained from the brown mass which remains after rectifying the ethylic anisoylacetate, by washing with ether and crystallising from hot chloroform and alcohol. It crystallises in very light, golden-yellow, iridescent leaflets, is easily soluble in chloroform, slightly so in hot alcohol, but insoluble in the other usual solvents; with concentrated sulphuric acid, it gives a yellowish-red solution, which, on heating, becomes brown with a green fluorescence, and finally colourless; with ferric chloride in alcoholic solution, it gives a purple-red coloration. It dissolves in cold ammonia, and the solution, when evaporated, yields the unchanged substance. When the ammoniacal solution is neutralised with nitric acid and silver nitrate added, a yellow precipitate, which is soluble in ammonia and not affected by light, is obtained.

E. W. W.

Amides of two substituted Orthoaldehydo-acids. By AUGUSTIN BISTRZYCKI and ENRIQUE FYNN (*Ber.*, 1898, 31, 922—929).—The substance obtained by the action of phosphorus pentachloride on bromopianic acid, which was described by Tust (*Abstr.*, 1892, 1209) as a trichloride, $\text{COCl} \cdot \text{C}_6\text{HBr}(\text{OMe})_2 \cdot \text{CHCl}_2$, is in reality the monochloride, $\text{COCl} \cdot \text{C}_6\text{HBr}(\text{OMe})_2 \cdot \text{CHO}$, and melts at 98—99°. On treatment with ammonia, it yields the amide, which, after crystallisation from chloro-

form, melts at 200° , whilst Tust gives 180° as the melting point after recrystallisation from water. The amide readily reacts with hydroxylamine hydrochloride, two products being formed. The first of these has the composition of the normal oxime, and crystallises in needles which melt and decompose at 267° ; when heated with acetic anhydride, however, it simply yields an *acetyl* derivative, melting at 242° , and not bromopiazone, $C_6HBr(OMe)_2 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CH} : \text{N} \end{smallmatrix}$, as might have been expected;

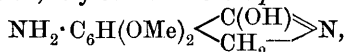
it seems probable, therefore, that this compound is not, in reality, a simple oxime. The second product, $C_{10}H_8NBrO_5$, crystallises in fascicular groups of needles melting at 227° , and is an oxidation product; it yields an *acetyl* derivative, which crystallises in tablets and melts at 159° . *Bromopiazone*, which is readily obtained by the action of hydrazine sulphate on bromopianic acid, crystallises in colourless, matted needles melting at $231-232^{\circ}$; its *acetyl* derivative also forms colourless needles melting at 173° . Bromopianic amide itself does not yield an anhydride when it is treated with acetic anhydride, but is converted into a *diacetyl* derivative, $C_{10}H_8BrNO_4Ac_2$, which crystallises in needles melting at 150° .

Nitro-opianic chloride, $NO_2 \cdot C_6H(OMe)_2(CHO) \cdot COCl$, forms faintly yellow, lustrous plates melting at $137-138^{\circ}$. The corresponding *amide* crystallises in yellow, lustrous needles, which melt and decompose at 203° ; this compound behaves towards hydroxylamine in a precisely similar manner to the bromopianic amide, and the compound produced crystallises in yellow needles which melt and decompose at 265° , whilst the *acetyl* derivative crystallises in tablets, and decomposes at 246° .
A. H.

Condensation Products from the Amides of two Orthoaldehydo-acids. By AUGUSTIN BISTRZYCKI and EDWARD FINK (*Ber.*, 1898, 31, 930-936. Compare the foregoing abstract).—Bromopianic amide is converted by phosphorus oxychloride into *bisbromometa-opindolone*,

$C_6HBr(OMe)_2 \begin{smallmatrix} \text{CO} \cdot \text{N} - \text{N} \cdot \text{CO} \\ | \quad | \\ \text{CH} \cdot \text{CH} \end{smallmatrix} C_6HBr(OMe)_2$, which forms a very sparingly soluble, brownish powder, and can be heated to 325° without undergoing any change. By reduction with tin and hydrochloric acid, it is converted into *dihydrobisbromometa-opindolone*, $C_{20}H_{18}N_2Br_2O_6$, a white, amorphous mass, and *bromohemipinic isoimidine*, $C_6HBr(OMe)_2 \begin{smallmatrix} \text{C(OH)} \\ \text{CH}_2 \end{smallmatrix} \text{N}$, which crystallises in white needles melting at 203° ; this compound yields an *acetyl* derivative, $C_{12}H_{16}NBrO_4$, which crystallises in small, white needles melting at $177-178^{\circ}$.

Bisnitrometa-opindolone, $(C_{10}H_8N_2O_5)_2$, is prepared in a similar manner to the bromo-derivative, which it closely resembles in properties. On reduction, it yields *amidohemipinic isoimidine*,



the hydrochloride of which forms small, white needles; the free base crystallises in small prisms melting and decomposing at $223-224^{\circ}$, whilst the *diacetyl* derivative crystallises in white needles and decomposes at 242° . Amidohemipinic isoimidine can readily be converted

into the bromo-compound described above by means of the diazo-reaction, and this proves that, in bromopianic acid, the bromine atom occupies the same position in the ring as the nitro-group of nitro-opianic acid, which is known to have the constitution $[\text{COOH} : \text{CHO} : (\text{OMe})_2 : \text{Br} = 1 : 2 : 5 : 6 : 3]$.
A. H.

Derivatives of Orthosulphobenzoic Anhydride. By MICHAEL DRUCK SOHON (*Amer. Chem. J.*, 1898, 20, 257—278).—Orthosulphobenzoic anhydride, obtained by the action of phosphorus pentachloride on the acid potassium salt or by distilling the acid with phosphoric anhydride, forms clear, colourless, monoclinic, deliquescent crystals, melts at 129.5° , sublimes at or below its melting point, and can be distilled. Alcohols dissolve it with formation of the acid salts of orthosulphobenzoic acid. The *methylic* and *ethylic* hydrogen salts, and also their *silver* and *potassium* salts, are described.

Phenols act on the anhydride at a temperature of 130 — 135° with the production of sulphonphthaleins, which decompose on heating to a slightly higher temperature (about 150°) with evolution of hydrogen sulphide and formation of darker and less soluble products, which were not further investigated. No evidence of the formation of benzoyl-benzenesulphonic acids could be obtained. The sulphonphthaleins are intensely coloured substances, more soluble in water than the corresponding derivatives of phthalic acid, and soluble in alcohol, from which they can be obtained crystalline by precipitation with ether.

Phenolsulphonphthalein, $\text{SO}_2 \langle \text{C}_6\text{H}_4 \rangle \text{O} \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2$, is precipitated as a bright red, crystalline powder, but on slow evaporation of a glacial acetic acid solution, it separates in distinct nodules of radiating needles, appearing blue-green by reflected and deep red by transmitted light; it is about as sensitive to acids and alkalis as phenolphthalein, the colour of the alkaline solution varying from red to purple. When treated with zinc dust in alkaline solution, small, granular crystals of *phenolsulphonphthalin* are formed, and with bromine in glacial acetic acid solution, it yields *dibromophenolsulphonphthalein* as a granular, purplish, crystalline powder. It gives a yellow solution with acids, and a blue to purple coloration with alkalis; it is extremely delicate as an indicator, being sensitive to ammonia but not to carbonic anhydride.

Phenolsulphonphthalein does not give an acetyl derivative, and when fused with potash is converted into a sulphite, phenol, and para-dihydroxybenzophenone.

Orthocresolsulphonphthalein, $\text{C}_{21}\text{H}_{18}\text{SO}_5$, separates from water in crystals, appearing bottle-green by reflected and deep carmine by transmitted light; its neutral or slightly acid solution is yellow, but with alkalis it gives a purple to carmine colour. With bromine, it forms a *dibromo*-derivative, and it can be acetylated.

Paracresolsulphonphthalein was not obtained pure; it has a yellow colour, and is somewhat fluorescent.

Resorcinolsulphonphthalein, $\text{SO}_2 \langle \text{C}_6\text{H}_4 \rangle \text{O} \text{C} \langle \text{C}_6\text{H}_3(\text{OH})_2 \rangle \text{O}$, is a

bright reddish-yellow powder, intensely fluorescent in alkaline solution. The bromine derivative is not as intense in colour as eosin.

Orcinolsulphonphthalein is easily produced, and has been already described by Gilpin (*Amer. Chem. J.*, 16, 528).

Quinolsulphonphthalein was obtained as a dark-brown mass, *pyrogallolsulphonphthalein* (*sulphongallein*) as a bluish-brown powder, *meta-amidophenolsulphonphthalein* as a reddish-brown powder, and the corresponding *para*-compound as a dark-coloured mass. Salicylic acid, when melted with the anhydride, gives a bright red colouring matter.

Ammonium benzaminesulphonate, obtained by the action of ammonia on the anhydride, crystallises from alcohol in needles melting at 256—257°. The corresponding *barium* and *potassium* salts are also described.

A similar reaction is given with aniline and the toluidines, with production of a salt of the base with a benzanilido-acid. The free acids are exceedingly soluble, and could not be obtained in a crystalline form, but the salts crystallise slowly from concentrated solutions. They are decomposed by boiling with acids or alkalis, yielding the base and orthosulphobenzoic acid, and with phosphorus pentachloride the corresponding sulphinide derivative is obtained.

Aniline benzanilidosulphonate separates from alcohol in white tufts of radiating needles. The *barium*, *ammonium*, *potassium*, *cadmium*, *sodium*, *copper*, *silver*, and *lead* salts are also described, from the last of which the *free acid* was obtained as a syrup by means of hydrogen sulphide.

Paratoluidine benzoparatoluido-orthosulphonate forms clusters of short, sharply-pointed needles, and the corresponding *orthotoluidine*-derivative, nodules of radiating needles. The *barium* and *potassium* salts are described.

The anhydride acts on acetamide and benzamide as a dehydrating agent, giving rise to the corresponding nitrile and orthosulphobenzoic acid; and with phosphorus pentachloride produces both chlorides of orthosulphobenzoic acid, excess of the reagent, continued action, and high temperature favouring the formation of the unsymmetrical chloride.

A. W. C.

Paramethoxyorthosulphobenzoic Acid. By P. R. MOALE (*Amer. Chem. J.*, 1898, 20, 288—298).—*Paramethoxyorthosulphobenzoic acid*, $\text{COOH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{SO}_3\text{H} + 2\frac{1}{2}\text{H}_2\text{O}$, prepared from paratoluidine-orthosulphonic acid according to the directions of Parks (*Abstr.*, 1893, i, 585), crystallises from water in long, transparent, colourless needles melting at 104°. When heated in a test-tube to 145°, it lost water, and fine needles sublimed, but could not be obtained in sufficient amount for analysis. The *potassium*, *calcium*, *magnesium*, and *lead* salts are described.

When heated together with resorcinol, *paramethoxysulphonefluorescein* is obtained as a reddish, granular mass which dissolves in alkalis with a beautiful, reddish-green fluorescence; neither this nor the corresponding *orcinol* compound could be obtained quite pure. With phenol, a dirty-brown mass is formed, with which it was found impossible to deal satisfactorily.

A. W. C.

Decomposition of Paradiazio-orthotoluenesulphonic Acid with Absolute Methylic Alcohol in presence of other Substances. By P. R. MOALE (*Amer. Chem. J.*, 1898, 20, 298—302).—When paradiazio-orthotoluenesulphonic acid is acted on with sodium methoxide in methylic alcohol solution, and the product treated respectively with phosphorus pentachloride and ammonia, orthotoluenesulphonamide is obtained in small amount, showing that the alkali causes the "hydrogen reaction" to take place to some extent. The residue is a black, tarry mass with which nothing could be done.

No definite results were arrived at when the decomposition was carried out with sodium ethoxide or caustic potash in ethylic alcohol solution, but by the action of dry ammonia gas in absolute methylic alcohol solution, and subsequent treatment of the residue with phosphorus pentachloride and ammonia, the amide of paratoluidine-orthosulphonic acid was obtained.

With aniline and methylic alcohol, three reactions take place according to the proportions of the reacting substances, one common product, and apparently three or four dyes, being formed.† A. W. C.

Silver Paraphenolsulphonate. By FRANCESCO ZANARDI (*Chem. Centr.*, 1897, ii, 547; from *Boll. Chim. Farm.*, 36, 449—452).—Paraphenolsulphonic acid is obtained as a thick syrup by decomposing barium paraphenolsulphonate with the calculated quantity of sulphuric acid. The aqueous solution of the acid, when treated with silver carbonate and evaporated at 20—25°, yields slender, white, prismatic needles of the silver salt; this is odourless, dissolves in 3 parts of water and in 80 parts of alcohol, and is insoluble in ether, chloroform, and carbon bisulphide; it is acted on by light, decomposes at 120°, and might be used as a disinfectant. E. W. W.

Parabenzoyldiphenylsulphone. By LYMAN C. NEWELL (*Amer. Chem. J.*, 1898, 20, 302—318).—Paratolylphenylsulphone prepared from paratoluenesulphonic chloride by Friedel and Craft's reaction, forms hexagonal plates melting at 124—125°. When oxidised with chromic acid in glacial acetic acid solution, it yields *paraphenylsulphonebenzoic acid*, crystallising from alcohol in small, white prisms melting at 273° (uncorr.), and not at above 300° as stated by Michael and Adair (*Abstr.*, 1878, 415). The *calcium*, *barium*, and *sodium* salts are described. The free acid and its salts are readily acted on by phosphorus pentachloride yielding *paraphenylsulphonebenzoic chloride*, $\text{SO}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$, which forms glistening, white plates, or short, white needles melting at 145.2—145.8°, and this substance, when treated with excess of concentrated ammonium hydroxide, is converted into *paraphenylsulphonebenzamide*, separating from alcohol in small transparent, acicular crystals melting at 242—243° (uncorr.); and with aniline it yields *paraphenylsulphonebenzanilide*, crystallising from alcohol in transparent, small prisms melting at 202—203° (uncorr.). *Parabenzoyldiphenylsulphone*, $\text{SO}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$, prepared from the chloride by the action of benzene in presence of aluminium chloride, crystallises from alcohol in fine, white, lustrous needles, which, when dry, pack together like felt, and melt at 133° (uncorr.). It may be recovered unchanged from its solution in warm, concentrated nitric acid,

or cold, concentrated sulphuric acid, and is not attacked by boiling alcoholic potash. On fusion with potash, it does not decompose into benzoic acid and diphenylsulphone like the corresponding ortho-compound (compare Remsen and Saunders, Abstr., 1895, i, 474), but the exact nature of the decomposition products could not be determined.

On treatment with phenylhydrazine, the sulphone yields a *phenylhydrazone*, $\text{NHPh}\cdot\text{N}:\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Ph}$, separating from alcohol in lustrous, lemon-yellow needles melting at 184° , and also a small amount of a substance, which appears to be acetophenylhydrazide. The formation of this substance can only be explained by supposing that the alcohol used in the experiment may have been oxidised to acetic acid, which may then have united with the excess of phenylhydrazine present. The corresponding *oxime* crystallises from alcohol in irregular leaflets melting at 201° .

The author has confirmed the work of Remsen and Saunders, who failed to obtain either an oxime or a phenylhydrazone from ortho-benzoyldiphenylsulphone. A. W. C.

Action of Phenyl- and Tolyhydroxylamines on Aromatic Thionylamines. By AUGUST MICHAELIS and KARL PETOU (*Ber.*, 1898, 31, 984—997).—A benzene solution of thionylaniline reacts with phenylhydroxylamine, yielding azobenzene and aniline phenylsulphonamate. Other thionylamines and β -substituted hydroxylamines react in a similar manner, 2 molecules of the former always reacting with 4 molecules of the latter. The reaction is a little more complex when the thionylamine and hydroxylamine contain different radicles, for example, $\text{R}\cdot\text{N}:\text{SO}$ and $\text{R}'\text{NH}\cdot\text{OH}$. When R and R' are similar, then the azo-compound is formed merely from the hydroxylamine, and has the symmetrical formula $\text{R}\cdot\text{N}:\text{N}\cdot\text{R}'$, a mixed sulphonamate, $\text{R}\cdot\text{NH}\cdot\text{SO}_3\text{NH}_3\text{R}'$, being formed at the same time. An exception to this is found in the reaction between parathionyltoluidine and phenylhydroxylamine, when the mixed azo-compound, benzene-azotoluene, is formed.

When the two radicles, R and R', are very different, then a mixed azo-compound is always formed, for example, when xyl-, ψ -cumyl- or naphthyl-thionylamines react with phenyl- or tolyl-hydroxylamines. These mixed azo-compounds are often red liquids, which can be purified by distillation in steam. In only one case, namely, by the action of paratolyhydroxylamine on metathionyltoluidine, was it found that the azo-compound was formed from the thionylamine, and had the symmetrical structure $\text{R}\cdot\text{N}:\text{N}\cdot\text{R}$, whilst a simple sulphonamate (2 mols.), $\text{R}'\cdot\text{NH}\cdot\text{SO}_3\cdot\text{NH}_3\text{R}'$, was formed at the same time.

A solution of phenylhydroxylamine (4 grams) in dry benzene (100 grams) readily reacts with thionylaniline (2.78 grams) also dissolved in benzene; after several hours, a crystalline mass of Wagner's aniline phenylsulphonamate (Abstr., 1886, 708) separates, and azobenzene remains dissolved in the benzene. Similarly, paratolyhydroxylamine (2 mols.) and thionylaniline (1 mol.) yield *paratoluidine phenylsulphonamate*, crystallising in white plates and melting at 236° , and an orange-yellow, crystalline azo-compound melting at 68 — 72° , probably orthotolueneazoparatoluene. Thionylaniline and orthotolyhydroxylamine

yield azo-orthotoluene and *orthotoluidine phenylsulphonamate*, which melts at 205° giving a bluish-purple liquid.

Thionylaniline and metatolyhydroxylamine yield *metatoluidine phenylsulphonamate*, which carbonises at 250°, and Jacobson's benzene azometatoluene (Abstr., 1896, i, 96).

Phenylhydroxylamine and parathionyltoluidine yield a mixture of sulphonamates melting at 223°, and benzeneazoparatoluene melting at 70—71°. Schultz (Abstr., 1884, 903), has previously described this compound as melting at 63°. Paratolyhydroxylamine and parathionyltoluidine yield paratoluene and *paratoluidine paratolylsulphonamate* melting at 210—211°. [In other parts of the paper this is stated to melt at 235—236°]. Orthotolyhydroxylamine and parathionyltoluidine yield *orthotoluidine paratolylsulphonamate* melting at 228°, and *orthoazoxytoluene*, $(C_7H_7)_2N_2O$, which crystallises from alcohol in yellow needles melting at 59°. Metatolyhydroxylamine and parathionyltoluidine yield *metatoluidine paratolylsulphonamate* melting at 225—226°, and metazotoluene melting at 54—55°. Orthothionyltoluidine and phenylhydroxylamine yield a mixture of sulphonamates melting at 238—239°, and Jacobson's benzeneazo-orthotoluene. Orthothionyltoluidine and paratolydroxylamine give *paratoluidine orthotolylsulphonamate*, melting at 241°, and paratoluene.

The same thionyl compound reacts with orthotolyhydroxylamine, yielding *orthotoluidine orthotolylsulphonamate*, melting at 212°, and orthoazotoluene, and with metatolyhydroxylamine yielding *metatoluidine orthotolylsulphonamate*, melting at 208°, and metazotoluene. Metathionyltoluidine and phenylhydroxylamine yield a mixture of sulphonamates and benzeneazometatoluene. The same thionyl compound reacts with paratolyhydroxylamine, yielding *paratoluidine paratolylsulphonamate*, melting at 235—236°, and metazotoluene. This is the only instance in which it has been found that the azo-compound is derived solely from the thionylamine. Metathionyltoluidine and orthotolyhydroxylamine yield a mixture of sulphonamates, melting at 219°, and Schultz's metatoluene-azo-orthotoluene. The same thionylamine and metatolyhydroxylamine yield *metatoluidine metatolylsulphonamate*, melting at 202°, and metazotoluene. Thionylmetaxylydine reacts with phenylhydroxylamine, yielding a mixture of sulphonamates and benzeneazometaxylylene; the latter is a red oil and is identical with the compound obtained by the action of nitrosobenzene on unsymmetrical metaxylydine.

Paratolueneazometaxylylene is obtained by the interaction of asymmetrical metathionylxylydine and paratolyhydroxylamine; when purified by distillation in steam and recrystallisation from alcohol, it forms yellowish-red, flat needles melting at 62°.

Thionylpseudocumidine reacts with phenylhydroxylamine, yielding a mixture of sulphonamates, melting at 218°, and *benzeneazopseudocumene*, which is a red oil. *Paratolueneazopseudocumene* crystallises in yellow needles melting at 58°. Benzeneazo- α -naphthalene, obtained from thionyl- α -naphthylamine and phenylhydroxylamine, crystallises from alcohol in small brick-red crystals melting at 70°; Nietzki and Zehntner (Abstr., 1893, i, 275) give the melting point as 63·5°. *Metatoluene-azo- α -naphthalene* melts at 43—44°.

Phenylhydroxylamine and thionyl-paraphenylenediamine react better in chloroform than in benzene solution; a crystalline sulphonamate, consisting probably of a mixture of aniline phenylsulphonamate and aniline paraphenylenedisulphonamate, is deposited, which carbonises between 200° and 300° without melting. The chloroform solution contains the *triaz*o-compound, $\text{PhN}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Ph}$, which, after recrystallisation from alcohol and sublimation, forms orange-red needles; it melts at $166\text{--}167^{\circ}$, and, when carefully heated, sublimes. Paratolylhydroxylamine, when treated in a similar manner, yields the *triaz*o-compound, $\text{N}_2(\text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me})_2$, melting at $201\text{--}202^{\circ}$. Both these compounds are sparingly soluble in alcohol or ether, somewhat more soluble in benzene, and readily soluble in chloroform. J. J. S.

Oxidation of Paranitrotoluenesulphonic Acid. By ARTHUR G. GREEN and ANDRÉ R. WAHL (*Ber.*, 1898, 31, 1078—1080. Compare this vol., i, 200).—In reply to the criticism of Ris and Simon (this vol., i, 322), the authors point out that the compound described by them as dinitrodibenzylsulphonic acid was in reality the free acid and not the sodium hydrogen salt as maintained by Ris and Simon. When a solution of normal sodium dinitrodibenzylsulphonate is acidified, the nature of the product depends on the conditions. Strong solutions yield the monosodium salt, dilute solutions the free acid. Solutions of intermediate strength yield the monosodium salt when slowly cooled, but when the liquid is quickly cooled, the free acid separates in plates which are converted into the monosodium salt by prolonged contact with the mother liquor. The authors also maintain the accuracy of their formula, $\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_{10}$, for the dinitrostilbenesulphonic acid, as against the formula, $\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_9$, proposed by Ris and Simon, and have further confirmed it by a quantitative reduction experiment, carried out with a weighed amount of zinc dust, the excess of zinc being afterwards estimated by Wahl's method (this vol., ii, 190). A. H.

Reduction of Aromatic Ketones by Sodium and Alcohol. By AUGUST KLAGES and PAUL ALLENDORFF (*Ber.*, 1898, 31, 998—1010).—Purely aromatic ketones, $\text{CRR}'\text{O}$, are reduced by sodium in boiling ethyl alcoholic solution to methane derivatives, $\text{CH}_2\text{RR}'$. Mixed aliphatic-aromatic ketones, $\text{CH}_3\cdot\text{CRO}$, are only reduced to carbinols, $\text{CH}_3\cdot\text{CHR}\cdot\text{OH}$; a little of the melthane derivative, $\text{CH}_3\cdot\text{CH}_2\text{R}$, is indeed obtained, but this is doubtless due to a secondary reaction, namely, the reduction of a styrene derivative, $\text{CH}_2\cdot\text{CHR}$, which is also present in small amount among the products of the reaction. Two purely aromatic ketones, tetramethyldiamidobenzophenone (Michler's ketone) and its tetrethyl analogue, resemble the mixed ketones in that they yield carbinols. The ketones used were prepared by condensing an acid chloride with an aromatic hydrocarbon in the presence of freshly prepared aluminium chloride (Friedel-Craft's reaction); light petroleum was found to be a suitable medium in which to effect this. In almost all the reactions described in the paper, the product was eventually distilled under diminished pressure. The substances obtained are enumerated below.

Diphenylmethane, CH_2Ph_2 . Parabenzyltoluene, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\text{Me}$. *Parabenzoylcumene*, $\text{CPhO}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}_2$, boils at $334\text{--}336^\circ$ under ordinary pressure, at $203\text{--}204^\circ$ under 20 mm., and has a sp. gr. = $1\cdot0364$ at $18^\circ/4^\circ$; *para-isopropylidiphenylmethane*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}_2$, boils at 310° under ordinary pressure, at 176° under 13 mm., and has a sp. gr. = $1\cdot007$ at $18^\circ/4^\circ$. Benzoylpseudocumene, $\text{CPhO}\cdot\text{C}_6\text{H}_2\text{Me}_3$, $[\text{Me}:\text{CPhO} = 1:2:4:5]$, boils at 328° under normal and at 211° under 23 mm. pressure, and has a sp. gr. = $1\cdot0332$ at $18^\circ/4^\circ$; *benzylpseudocumene*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_2\text{Me}_3$, boils at $308\text{--}312^\circ$ under ordinary pressure, at $190\text{--}191^\circ$ under 20 mm., and has a sp. gr. = $1\cdot0151$ at $18^\circ/4^\circ$. Benzoylmesitylene, $\text{CPhO}\cdot\text{C}_6\text{H}_2\text{Me}_3$, $[\text{Me}_3:\text{CPhO} = 1:3:5:2]$; benzylmesitylene, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_2\text{Me}_3$. Parethoxybenzophenone, $\text{CPhO}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, boils at 242° under 40 mm. pressure; *parethoxydiphenylmethane*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$,

boils at 317° , 217° , and 203° under ordinary pressure, 37 mm. and 12 mm. respectively, and could not be hydrolysed.

Tetramethyldiamidobenzhydrol, $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$. *Tetretlyldiamidobenzhydrol*, $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, melts at 78° , and yields, with hydroxylamine and sodium hydrogen carbonate in alcoholic solution, a substance which melts at $128\text{--}129^\circ$, and contains 11.6 per cent. of nitrogen.

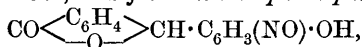
Phenylmethylcarbinol, $\text{CHMePh}\cdot\text{OH}$, boils at $203\cdot6^\circ$ (corr.) under $745\cdot4$ mm., at 118° under 40 mm., and has a sp. gr. = $1\cdot007$ at 21° ; the *benzoate* boils at 189° under 20 mm. pressure, and under pressures greater than 25 mm. breaks up more or less into styrene and benzoic acid; the *phenylcarbamate* melts at 94° . The ethylbenzene also obtained in the reduction of acetophenone when added to bromine to which a little aluminium has been added previously, yields a *tetrabromo*-substitution derivative melting at $138\text{--}139^\circ$. Acetylpsudocumene, $\text{C}_6\text{H}_2\text{Me}_3\text{Ac}$ $[\text{Me}_3:\text{Ac} = 1:2:4:5]$, boils at $137\text{--}138^\circ$ under 20 mm. pressure, and has a sp. gr. = $1\cdot001$ at $18^\circ/4^\circ$; its *oxime* melts at $85\text{--}86^\circ$; *trimethylphenethylol*, $\text{OH}\cdot\text{CHMe}\cdot\text{C}_6\text{H}_2\text{Me}_3$, $[\text{Me}_3:\text{CHMe} = 1:2:4:5]$, boils at $252\text{--}253^\circ$ with slight decomposition under ordinary pressure, at $140\text{--}141^\circ$ and 138° under 18 and 15 mm.; the *acetate* boils under the ordinary pressure at $254\text{--}257^\circ$ with slight decomposition, and at 130° under 13 mm.; the *phenylcarbamate* melts at 108° ; the *chloride* can be obtained, although only in an impure state, by treating the carbinol with phosphorus pentachloride at the ordinary temperature, or saturating it with gaseous hydrogen chloride at 0° ; it boils at $125\text{--}129^\circ$ under 13 mm. pressure, and loses hydrogen chloride when distilled under higher pressures. *1:2:4-Trimethyl-5-vinylbenzene*, $\text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_2\text{Me}_3$, is obtained when the above mentioned acetate is boiled with methyl alcoholic potash; it distils over at 97° under 22 mm. pressure, and leaves a residue of a *polymeride* (α), which, after crystallisation from alcohol and light petroleum, melts at 118° . Moreover, the boiling point of the substance itself under atmospheric pressure, originally $212\text{--}214^\circ$, rises as the distillation is repeated, partial polymerisation no doubt taking place; and if hydrogen chloride be removed from the above-mentioned chloride by warming it gently with aniline, or if the corresponding carbinol be warmed with syrupy phosphoric acid, a second

polymeride (β), melting at 163° , is obtained. The unpolymerised substance forms a *dibromide*, which melts at 65 – 66° . Acetylmesitylene has a sp. gr. = 0.985 at $18^\circ/4^\circ$. *Trimethylphenethylol*, [$\text{Me}_3\text{CHMe} = 1:3:5:2$], isomeric with the last carbinol, melts at 71° , and boils at 248° under ordinary pressure, at 141° under 24 mm.; the *acetate* boils at 252° under ordinary pressure, at 134 – 135° under 15 mm.; the *phenyl-carbamate* melts at 124° ; the (impure) *chloride* boils at 126 – 127° under 16 mm. pressure. *1:3:5-Trimethyl-2-vinylbenzene* is obtained when the last-mentioned carbinol is treated with phosphoric anhydride, but not when the acetate is boiled with methyl alcoholic potash; it boils at 208 – 210° without polymerising, but is converted by 80 per cent. sulphuric acid into a *polymeride* which melts at 62° , and boils and decomposes slightly at 178 – 180° under 19 mm. pressure. This *polymeride* is also obtained when the chloride is warmed with aniline, it remains behind in the flask when the product is distilled with steam, whilst a small quantity of the unpolymerised substance passes over.

C. F. B.

Dimethylanilinephthaloylic Acid. By HEINRICH LIMPRICHT [and E. KÖNIG] (*Annalen*, 1898, 300, 228–239).—*Dimethylanilinophthaloylic acid*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, is obtained by adding aluminium chloride in small quantities at a time to a solution of phthalic anhydride and dimethylaniline in carbon bisulphide, and subsequently heating the mixture for 3–4 hours in a reflux apparatus; it melts at 205° , and separates from alcohol in two forms, one of which is anhydrous, the other containing 1 mol. of alcohol. The *barium* salt dissolves readily in water, and the *silver* salt melts at about 180° to a black liquid; the *hydrochloride* forms thin leaflets, and melts to a reddish-brown liquid at about 190° . The *nitroso-derivative*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, contains $1\text{H}_2\text{O}$, which is removed at 112 – 120° , the anhydrous substance melting at 164° ; the *barium* salt forms red, prismatic crystals, which rapidly effloresce and become yellow on exposure to the air. Boiling caustic soda eliminates dimethylamine from the nitroso-derivative, giving rise to *nitrosophenolphthaloylic acid*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, which separates from ethylic acetate in bright yellow, prismatic crystals, and melts at 178° .

Dimethylanilinophthalide, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, is prepared by heating dimethylanilinophthaloylic acid with ammonia and zinc dust during 2 hours, and melts at 188° ; it dissolves in caustic soda, but is almost insoluble in boiling sodium carbonate. The *nitroso-derivative* melts at 157° , and yields *nitrosophenolphthalide*,



under the influence of hot caustic soda; the latter nitroso-compound melts at 153° , and yields a *barium* salt when dissolved in baryta.

Dimethylanilinohydrophthaloylic acid, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, produced on heating dimethylanilinophthaloylic acid with zinc dust and ammonia for 12 hours at 70 – 80° , melts at 173° ; the *barium* salt forms small, white prisms. The *nitroso-derivative* crystallises from alcohol, and melts at 133° .

M. O. F.

Triphenylethanone (Benzoyldiphenylmethane). By A. GARDEUR (*Chem. Centr.*, 1897, ii, 660—662; from *Bull. Acad. roy. Belg.*, [iii], 34, 67—100).—From triphenylethanone, $\text{CPh}_2\cdot\text{COPh}$, prepared by Delacré's method (*Compt. rend. Assoc. franc. Congrès de Pau*, 181) the author obtained the benzoyl derivative by heating it with benzoic chloride for 2—3 days at 240° , although attempts to prepare it by Saint Pierre's method (*Bull. Soc. Chim.*, [iii], 5, 292) failed. This compound does not combine with hydrogen bromide, yet its constitution probably corresponds with the enolic form, $\text{CPh}_2\cdot\text{CPh}\cdot\text{OBz}$, for when reduced with sodium amalgam in alcohol, it yields triphenylethylic alcohol, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{OH}$. When the benzoyl derivative was treated with alkali, however, either no reaction took place, or triphenylethanone of the ordinary ketonic form was produced. Delacré's sodium compound of triphenylethanone is a derivative of the ketonic type, for when heated with chlorobenzene, it yields triphenylmethane which can only result from the intermediate formation of tetraphenylethanone, $\text{CPh}_3\cdot\text{COPh}$. *Triphenylchlorethanone*, $\text{CPh}_2\text{Cl}\cdot\text{COPh}$, prepared by passing chlorine into an almost boiling solution of triphenylethanone in light petroleum, is a yellowish oil which, with water, forms triphenylethanolone, $\text{OH}\cdot\text{CPh}_2\cdot\text{COPh}$. This is best prepared, however, by heating triphenylbromethanone with silver benzoate for 24 hours at about 200° , and then hydrolysing the benzoate thus obtained. The benzoate crystallises from glacial acetic acid and alcohol in needles, and melts at 169° . By heating a solution of triphenylethanolone in glacial acetic acid with phenylhydrazine, small, crystalline needles of a substance which melts at 144° , and is probably the corresponding phenylhydrazone, are obtained. *Triphenylethanonephenylhydrazone*, which is prepared in a similar way, crystallises from glacial acetic acid in star-shaped needles, and melts at 156° . When triphenylbromethanone is reduced with zinc dust and glacial acetic acid, triphenylethanone and triphenylethylic alcohol, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{OH}$, are formed. The latter, when heated with benzoic chloride, forms a benzoate which crystallises from glacial acetic acid in needles, and melts at 145° . By the action of bromine in glacial acetic acid on triphenylethylic alcohol or its benzoate, *triphenylbromethylene*, $\text{CPh}_2\cdot\text{CBrPh}$, is obtained; this crystallises from glacial acetic acid in needles, melts at 115° and with hydrogen bromide forms an unstable additive compound which melts at $106\text{—}110^\circ$, and with water yields triphenylethanone of the ordinary ketonic form. *Triphenylchlorethylene* obtained by the action of phosphorus pentachloride on triphenylethanone, crystallises from alcohol in short cylinders, and melts at 117° ; when phosphorus pentabromide acts on triphenylethanone, triphenylbromethanone is formed. Triphenylethanedial (*triphenylethylenic glycol*), $\text{OH}\cdot\text{CPh}_2\cdot\text{CHPh}\cdot\text{OH}$, obtained in theoretical yield by the action of 10 times the calculated quantity of 7—8 per cent. sodium amalgam on a solution of triphenylethanolone in alcohol, crystallises in needles and melts at 164° ; the *diacetyl* derivative crystallises from glacial acetic acid, and melts at 214° . Attempts to obtain triphenylethanone of the enolic form by withdrawing water from the glycol by means of hydrogen chloride, hydrogen bromide, or zinc chloride, yielded only the ordinary triphenylethanone. In one experiment, however, in which the glycol was melted with zinc

chloride, an oil was formed whose alcoholic solution, after remaining for a few days, deposited needles which melted at 100—102°, and appeared to be a mixture of the ordinary triphenylethanone with another substance, although the former alone was obtained on recrystallisation. When triphenylethylenic glycol is reduced with zinc and acetic acid, triphenylethanone is formed. By the action of potassium hydroxide and sodium acetate on the glycol, or by keeping it in a molten condition for some time, benzaldehyde and benzhydrol are obtained; in addition to these products, *benzhydrol ether*, $O(CHPh_2)_2$, which crystallises from alcohol in needles and melts at 118°, is formed when the glycol is submitted to dry distillation.

Triphenylethylenic oxide, $O \begin{smallmatrix} \diagup CPh_2 \\ \diagdown CHPh \end{smallmatrix}$, prepared by the action of

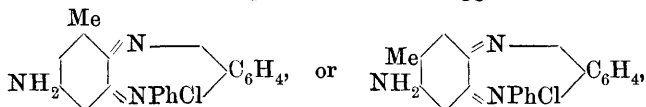
phosphoric anhydride on a solution of triphenylethylenic glycol in benzene, crystallises from glacial acetic acid in envelope-like crystals, melts at 105°, is stable in alkaline solutions, but in acid solutions or by recrystallisation is converted into the ordinary triphenylethanone.

E. W. W.

Aposafrafines and Azonium Compounds from Tolusafranine. By FRIEDRICH KEHRMANN and ALEXANDER WETTER (*Ber.*, 1898, 31, 966—977).—The amido-group is best removed from Geigy's tolusafranine chloride by the following process. A solution of the chloride (60 grams) in the requisite quantity of boiling water is treated with dilute sulphuric acid so that a crystalline mass is obtained; this is cooled to 0°, and then treated with a little more than the theoretical quantity of sodium nitrite in concentrated aqueous solution; the resulting dark blue diazo-solution is gradually added to an equal volume of alcohol, also cooled to 0°, and the alcohol distilled; sulphuric acid (5 c.c.) is added to the dark red liquid, and the mixture allowed to remain for 12 hours. A crystalline mass, consisting of about equal quantities of methyl- and dimethyl-aposafraanine derivatives, separates, and a considerable quantity of the dimethyl derivative remains in the mother liquor. The methylaposafranine is best purified by the aid of its chloride, which is much less soluble in dilute hydrochloric acid than the chloride of the dimethyl derivative. The separation is only completed after repeated solution in water and precipitation with dilute hydrochloric acid. *Methylaposafranine chloride*, $C_{19}H_{16}N_3Cl$, crystallises in long, pale yellow needles, is moderately soluble in water and readily in alcohol, yielding blood-red solutions; its alcoholic solution also exhibits a strong, light red fluorescence. Saturated aqueous solutions are completely precipitated on the addition of a few drops of dilute hydrochloric acid. Alkalis precipitate the base, but carbonates in dilute solution do not do so. Both in physical and chemical properties, the chloride resembles ros-induline chloride. The *nitrate* is also sparingly soluble in water, but practically insoluble in dilute nitric acid; the *platinochloride*, $(C_{19}H_{16}N_3)_2PtCl_6$, crystallises in small, reddish-brown plates, and is practically insoluble in water. The *acetyl* derivative of the chloride crystallises in long, yellowish-brown needles, which are soluble in water or alcohol, yielding yellowish-red solutions; the acetyl deriva-

tive differs completely from the corresponding derivative of aposafranine chloride (Abstr., 1896, i, 323). It yields very little amido-derivative, or tolosafranine chloride, when its alcoholic solution is allowed to remain in contact with ammonia for several days at the ordinary temperature, being merely hydrolysed. Aniline only reacts with the acetyl derivative when kept in contact with it for 14 days. The *platinochloride* of the acetyl derivative, $(C_{22}H_{20}N_3O)_2PtCl_6$, and the *nitrate*, $C_{22}H_{20}N_4O_4 + H_2O$, are described.

On account of the similarity between methylaposafranine and ros-induline, one of the following constitutions is suggested for the former,



in both of which the quinoid double bonds are on the heavier or basic side of the molecule. Monomethylaposafranine chloride is readily diazotised when suspended in 10 per cent. hydrochloric acid and treated with sodium nitrite; the diazotisation requires a longer time when a more dilute acid is employed. *Phenyltoluophenazonium* is obtained as its *iron double salt*, $C_{19}H_{15}N_2FeCl_4$, when the chloride is diazotised and the diazo-solution added to alcohol, and, at the end of 2 hours, precipitated with a saturated solution of ferric chloride in dilute hydrochloric acid, and may be best purified by washing with glacial acetic acid and subsequent crystallisation from the same solvent; it forms thick, brownish-red prisms melting at 150° , and dissolves readily in cold water and in hot acetic acid. The *nitrate*, $C_{19}H_{15}N_2 \cdot NO_3$, obtained by precipitating the iron with ammonium carbonate, then adding dilute nitric acid, and salting out with solid sodium nitrate, also forms reddish-brown crystals. When the iron double salt is dissolved in alcohol (80 per cent.), and then treated with an excess of concentrated aqueous ammonia, a mixture of two isomeric methylaposafranines is obtained; the chief product is the methylaposafranine already described, but a small quantity of an isomeric substance is also formed, the chloride of which is more soluble in water, and crystallises in bronzy, glistening needles.

It is practically impossible to isolate pure dimethylaposafranine from Geigy's compound; even after repeated crystallisation, it always contains a quantity of the monomethyl derivative. When the impure dimethyl derivative is treated in the manner described above for the monomethyl derivative, a mixture of the double iron salts of methyl- and dimethyl-phenylphenazonium chlorides is formed. The dimethyl compound, $C_{20}H_{17}N_2FeCl_4$, is readily freed from the monomethyl compound, as it is much less soluble in glacial acetic acid; it crystallises in large, pale brown plates melting at 190° , and is readily soluble in water, but only sparingly in alcohol or acetic acid. The *nitrate*, $C_{20}H_{17}N_2 \cdot NO_3$, and *platinochloride*, $(C_{20}H_{17}N_2)_2PtCl_6$, are also described. A concentrated solution of the iron double salt in alcohol (80 per cent.), when treated with an excess of concentrated ammonia and allowed to remain for 24 hours, yields *dimethylaposafranine*, the chloride of which crystallises in dark brown needles; its solutions in water or alcohol

have a magenta-red colour, and the latter exhibits a bright red fluorescence. The *platinochloride*, $(C_{20}H_{18}N_3Cl)_2PtCl_4$, and *acetyl derivative* are described. J. J. S.

Change of Position of the Double Linkings in Azonium Derivatives and its Causes. By FRIEDRICH KEHRMANN (*Ber.*, 1898, 31, 977—984).—Numerous facts seem to indicate that the quinoid double-bonds in azonium compounds can change their position; this supposition is rendered absolutely necessary if it be conceded that amines and alkalis always react with azonium compounds yielding derivatives with the substituting groups in the quinoid nucleus (that is, in the benzene ring to which the double bonds are attached). The latter conclusion receives support from the fact that quinones themselves react with amines, yielding derivatives in which the substituting groups are attached to the same benzene nucleus as that to which the quinone oxygen atoms are attached.

The author compares the change in position of the quinoid bonds in azonium compounds to the mutual oxidation and reduction of quinones and quinols, the reaction being regarded as an intramolecular oxidation and reduction. It is shown that the same generalisations hold for the two cases. Several examples are given in illustration of the change in position of double linkings. J. J. S.

2:4-Tetrachloro-1:3-diketotetrahydronaphthalene. By E. C. THEODOR ZINCKE and G. EGLY (*Annalen*, 1898, 300, 180—205).—

2:4-Tetrachloro-1:3-diketotetrahydronaphthalene, $C_6H_4 \begin{array}{c} \text{CO} \cdot \text{CCl}_2 \\ | \\ \text{CCl}_2 \cdot \text{CO} \end{array}$, is obtained as a hydrate by passing chlorine into a suspension of the anilide, $C_6H_4 \begin{array}{c} \text{C}(\text{NHPh}) \cdot \text{CCl} \\ | \\ \text{CCl} \text{---} \text{C} \cdot \text{OH} \end{array}$ (Zincke and Kegel, *Abstr.*, 1889, 268), in glacial acetic and hydrochloric acids. The *hydrate*, which contains $3H_2O$, is also produced by the action of chlorine on 1:3-dihydroxynaphthalene, and crystallises in thin, colourless plates; it sinters at 80° , melts to a clear liquid at about 90° , and intumesces at 100° . The anhydrous ketochloride, which is formed on exposing the hydrate to a vacuum, or to a temperature of 100 — 110° , crystallises in stellate groups of prisms, and melts at 92° .

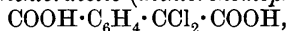
The *methoxy-compound*, $C_6H_4 \begin{array}{c} \text{C}(\text{OH})(\text{OMe}) \cdot \text{CCl}_2 \\ | \\ \text{CCl}_2 \text{---} \text{C}(\text{OH})_2 \end{array} \cdot H_2O$, is obtained by boiling a solution of the hydrate in methylic alcohol; it begins to sinter at 86° , melts to a clear, red liquid at 156° , and decomposes at 160° .

2:4-Dichloro-1:3-dihydroxynaphthalene (*dichloronaphtharesorcinol*), $C_6H_4 \begin{array}{c} \text{C}(\text{OH}) \cdot \text{CCl} \\ | \\ \text{CCl} \text{---} \text{C} \cdot \text{OH} \end{array}$, prepared by heating a solution of the hydrate in glacial acetic acid with concentrated hydrochloric acid and stannous chloride, crystallises from glacial acetic acid in colourless needles or nacreous leaflets, and melts at 138 — 139° . The *diacetyl derivative* melts at 136° . Phenylhydrazine gives rise to the *compound*, $C_6H_4 \begin{array}{c} \text{C}(\text{OH}) \text{---} \text{CCl} \\ | \\ \text{C}(\text{N} \cdot \text{NPh}) \cdot \text{C} \cdot \text{OH} \end{array}$, which melts at about 190° ; the *diacetyl derivative* melts at 150° .

Orthodichloroacetylphenyldichloroacetic acid, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CCl}_2 \cdot \text{COOH}$, obtained by the action of sodium carbonate on the ketohydrate, crystallises from benzene in colourless needles and small prisms, and melts at $106-107^\circ$. The *methylic* salt forms colourless needles, and melts at $114-115^\circ$. On heating the acid or the ketohydrate with sodium carbonate, β -dichloro- α -ketohydroxyhydrindenecarboxylic acid, $\text{CO} < \begin{smallmatrix} \text{CCl}_2 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}(\text{OH}) \cdot \text{COOH}$ (Zincke and Gerland, Abstr., 1888, 1199), is produced.

Orthotrichloroacetylphenyldichloroacetic acid, $\text{CCl}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CCl}_2 \cdot \text{COOH}$, is prepared by treating the ketohydrate with a solution of bleaching powder; it crystallises from benzene in colourless needles, or in monoclinic plates and melts at 135° , beginning to decompose at $150-160^\circ$. The *sodium* salt forms needles, and the *methylic* salt melts at $108-109^\circ$; the *anhydride* sublimes at 160° and melts at 224° , yielding dichloromethylenephthalyl. The action of hot sodium carbonate converts the acid into *trichloroacetophenonecarboxylic acid*, $\text{CCl}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, which melts at 139° ; alkalis eliminate chloroform. The *hydroxylactone* of orthotrichloroacetylphenyldichloroacetic acid, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{C}(\text{OH})(\text{CCl}_3) \cdot \text{O} \\ \text{CCl}_2 \end{smallmatrix} \text{CO}$, is produced on boiling the acid with water, and forms large, monoclinic crystals; it melts and decomposes at 139° . The *acetyl* derivative crystallises from benzene in colourless prisms, melting at 170° . The hydroxylactone yields dichloromethylenephthalyl (Zincke and Cooksey, Abstr., 1890, 784) when heated with sodium acetate.

Orthocarboxyphenyldichloroacetic (dichlorohomophthalic) acid,



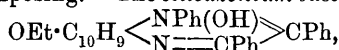
obtained on the action of potash on orthotrichloroacetylphenyldichloroacetic acid dissolved in methylic alcohol, crystallises from hot, dilute nitric acid in white needles, and from benzene in colourless plates melting at 141° , with formation of the *anhydride*, which melts at 130° . Aqueous alkalis convert the acid into orthocarboxybenzoylformic acid.

M. O. F.

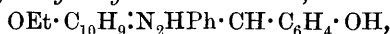
Reduction Products of Azo-compounds. VIII. By PAUL JACOBSON and ANDREW TURNBULL (*Ber.*, 1898, 31, 890—906. Compare Abstr., 1896, i, 23).—It has previously been shown that whereas benzeneazophenetoil readily yields an orthosemidine on reduction with a hydrochloric acid solution of stannous chloride, benzeneazo-metacresetoil undergoes the same transformation much less readily, the difference having been ascribed to the presence of the methyl group in the ortho-position relatively to the azo-group. On the other hand, Witt and Helmholtz have found (Abstr., 1894, i, 606) that benzeneazo- α -naphthyl ethylic ether very readily yields an orthosemidine derivative when it is reduced with stannous chloride, and the product then treated with hydrochloric acid. The authors have applied this method of reduction to all three compounds, and have found that, under these circumstances also, the orthosemidine forms 81 per cent. of the total semidine derivatives obtained from benzeneazophenetoil, 50 per cent. of the total obtained from benzenazometacresetoil, and 100 per cent. of that from benzeneazonaphthyl ethylic ether; thus showing that the reaction is not influenced by the substitution of the naphthalene ring for the

simpler benzene ring. Benzeneazo-*ar*-tetrahydronaphthyl ethylic ether, however, behaves in a similar manner to the metacresetol derivative, the orthosemidine amounting to only 50 per cent. of the total semidines obtained. The reduced ring of the naphthalene molecule, therefore, exerts an influence similar to that of a methyl group. Benzeneazo-*ar*-tetrahydronaphthyl ethylic ether, $\text{PhN}_2 \cdot \text{C}_{10}\text{H}_9 \cdot \text{OEt}$, prepared by the action of sodium ethoxide and ethylic iodide on the corresponding naphthol, crystallises in orange-red prisms which have a golden lustre and melt at 91.5° . That this compound actually has the constitution assigned to it, is shown by the fact that benzeneazo-*ar*-tetrahydronaphthol, from which it is prepared, is converted by reduction, followed by oxidation, into tetrahydro- α -naphthaquinone. On reduction, it yields the ortho- and para-semidine derivatives, as well as a smaller amount of *paramido-ar-tetrahydronaphthyl ethylic ether*, which crystallises from light petroleum in long, colourless needles melting at 60° . The orthosemidine derivative, 4-amido-3-anilido-1-ethoxy-1':2':3':4'-tetrahydronaphthalene,

$\text{C}_6\text{H}_5 \begin{smallmatrix} \text{C}(\text{OEt}) : \text{CH} \\ \text{C}(\text{NH}_2) : \text{C} \end{smallmatrix} \text{NHPH}$, crystallises from light petroleum in colourless plates or needles, which become pink on exposure to the air and melt at $168-169^\circ$. The corresponding *azimide*, $\text{OEt} \cdot \text{C}_{10}\text{H}_9 \begin{smallmatrix} \text{NPh} \\ \text{N} \end{smallmatrix}$, crystallises in colourless, oblique tablets, melts at $125-126^\circ$, and can be sublimed without decomposing. The *stilbazonium* base,



forms yellow prisms and melts at 151.5° . The *methenyl* compound, $\text{OEt} \cdot \text{C}_{10}\text{H}_9 \begin{smallmatrix} \text{NPh} \\ \text{N} \end{smallmatrix} > \text{CH}$, which is obtained by heating the base with formic acid, crystallises in thin plates melting at 139° , and yields a sparingly soluble nitrate. The carbon bisulphide derivative, $\text{OEt} \cdot \text{C}_{10}\text{H}_9 \begin{smallmatrix} \text{NPh} \\ \text{N} \end{smallmatrix} > \text{C} \cdot \text{SH}$, is only slowly formed and melts at $269-270^\circ$, whilst the *orthohydroxybenzylidene* derivative,



prepared from salicylaldehyde, crystallises in yellow prisms melting at $130-131^\circ$. The orthosemidine is converted by oxidation with ferric chloride into *anilidotetrahydro- α -naphthaquinone*, $\text{C}_6\text{H}_5 \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{CO} \cdot \text{NHPH} \end{smallmatrix}$ which forms brownish-red crystals melting at 164° .

The parasemidine derivative, *paramidophenylparethoxytetrahydro- α -naphthylamine*, $\text{C}_6\text{H}_5 \begin{smallmatrix} \text{C}(\text{OEt}) = \text{CH} \\ \text{C}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2) \end{smallmatrix} > \text{CH}$, crystallises in colourless prisms, melts at $87-88^\circ$, and becomes bluish on exposure to the air. The *sulphate* is only very sparingly soluble in water, whilst the *hydrochloride* dissolves more readily. This base gives the characteristic reactions of a parasemidine with nitrous acid, ferric chloride, chromic acid, and lead peroxide. The *monacetyl* derivative, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$, crystallises in colourless needles melting at $177-178^\circ$, and the thiocarbamide, $(\text{OEt} \cdot \text{C}_{10}\text{H}_9 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH})_2\text{CS}$, crystallises in plates melting at 201° .

Tetrahydronaphtholdis-azobenzene, $\text{OH} \cdot \text{C}_{10}\text{H}_9(\text{N}_2\text{Ph})_2$, is formed in the preparation of benzeneazo-*ar*-tetrahydro- α -naphthol, and melts at 156° .
A. H.

Orientation in the Terpene Series : Conversion of Monocyclic Terpenes into the corresponding Derivatives of Benzene. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1898, 31, 1401—1405).—The authors have devised a general method by which monocyclic terpenes may be converted into the corresponding derivatives of benzene; it depends on the ultimate bromination of the terpene dihydrobromide, followed by reduction of the product with zinc and hydrochloric acid. It is found more convenient to brominate the dihydrobromides with bromine in presence of iodine, it being then unnecessary to raise the temperature as in using the halogen in presence of iron.

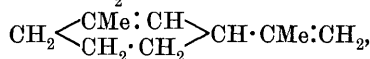
On this principle, paracymene and metacymene have been obtained from limonene and carvestrene respectively.

The passage from carone to carvestrene is now explained. Caronic acid has been recently synthesised by Perkin and Thorpe (*Proc.*, 1898, 107), in a manner which proves that it has the constitution assigned to it by von Baeyer (*Abstr.*, 1897, i, 83). The production

of dihydrocarvone, $\text{CHMe} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$, from carone

$\text{CHMe} \cdot \text{CO} \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{CMe}_2$, on the one hand, and the conversion of

carylamine, $\text{CHMe} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{CMe}_2$, into carvestrene,



on the other, represent the two directions which the rupture of the trimethylene ring is capable of following.

M. O. F.

Action of Sulphuric Acid on *l*-Terebenthene. By GUSTAVE BOUCHARDAT and J. LAFONT (*Compt. rend.*, 1897, 125, 111—114).—By the action of sulphuric acid on *lævo*-terebenthene, and subsequent treatment with alcoholic potash, a number of products are obtained, among which are two potassium salts both readily soluble in water. The less soluble of the two, *potassium terebenthene sulphate*, $\text{C}_{10}\text{H}_{16}\text{SHKO}_4$, crystallises in colourless plates somewhat resembling boric acid. Its rotatory power in alcoholic solution is $[\alpha]_D = -25$. Its aqueous solution is stable in the presence of a little alkali, but in neutral or acid solution readily undergoes decomposition, yielding potassium hydrogen sulphate and *l*-borneol. Nitric acid oxidises it to *l*-camphor melting at 203° . The second potassium salt has the same composition, but crystallises in silky needles, and its rotatory power is $[\alpha]_D = +10^\circ$. It is decomposed in neutral or acid aqueous solution, yielding sulphuric acid and the alcohol melting at 45° , previously called isoborneol, but which the authors state to be *d*-fenchol. Nitric acid oxidises this potassium salt or the alcohol obtained from it to liquid camphor, identical with that obtained by the oxidation of synthetical isoborneol.

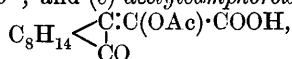
J. J. S.

Ethereal Oil of Pine Wood. By PETER KLASON (*Bied. Centr.*, 1898, 27, 137—138; from *Svensk. kem. tidskr.*, 1897, 9, 138—140).—The oil obtained by the steam distillation of pine resin was found to be almost pure pinene. On the other hand, the oil extracted from pine wood by means of acid sulphite solution proved to be cymene. No terpenes are present in pine wood oil. N. H. J. M.

A Crystalline Dicumphene Hydride. By ALEXANDRE ÉTARD and GEORGES MEKER (*Compt. rend.*, 1898, 126, 526—529).—Terbenthene hydrochloride (100 parts) is heated until it just melts, sodium (15 parts) is introduced in one lot and the mixture well shaken so as to granulate the molten sodium; the reaction should take place slowly and at as low a temperature as possible. When the reaction is complete, the mixture is extracted with benzene and then fractionated, when two portions, one distilling at 150—160°, and a second at 320—330°, are obtained. The heavier fraction is mixed with a little benzene and agitated with fuming sulphuric acid. After well washing first with Nordhausen, then with concentrated sulphuric acid, and finally with water, the substance is distilled, when, if the liquid is well cooled, 15—20 per cent. of a crystalline substance is obtained. These crystals consist of *dicumphene hydride*, $C_{20}H_{34}$, and belong to the regular system, sp. gr. = 1.001 at 15°; it melts at 75°, boils at 326—327° (uncorr.), and has specific rotatory power $[\alpha]_D = +15^\circ 27'$. [Letts obtained in this way a crystalline dicumphene hydride, $C_{20}H_{34}$, melting at 94°, and boiling at 321—323.6° (Abstr., 1880, 669); to this no reference is made.—A. J. G.] J. J. S.

The Rhodinol Question. By JULIUS BERTRAM and EDUARD GILDEMEISTER (*Ber.*, 1898, 31, 749).—Poleck has no right to complain (this vol., i, 263) that the name of *geraniol* has been substituted for his name of *rhodinol*. What Eckart called rhodinol was a mixture of 70 per cent. of geraniol with 20 of *l*-citronellol and 10 of non-alcoholic substances of unknown composition. C. F. B.

Action of Ethylic Oxalate on Camphor. III. By J. BISHOP TINGLE (*Amer. Chem. J.*, 1898, 20, 318—342. Compare Trans., 1890, 652; Abstr., 1897, i, 484).—When camphoroxalic acid is boiled with acetic anhydride, there are produced, in small amounts, (a) a substance crystallising in clusters of colourless, slender needles melting at 242—242.5°, the nature of which has not been ascertained; (b) a substance, probably an anhydride, crystallising from light petroleum in slender needles melting at 190°; and (c) *acetylcamphoroxalic acid*,



crystallising from benzene in reticulated, stellate, needle-shaped prisms melting at 133.5—134.5°. It reacts speedily with bromine vapour, liquefying, and then gradually giving off hydrogen bromide, but no crystalline compound could be obtained.

Bromine vapour acts on camphoroxalic acid, producing a *bromo-acid*, $C_{12}H_{15}O_4Br$, as an oil which gradually solidifies to crystalline nodules melting at 130°. The *silver* and *copper* salts are described. Magnesium amalgam removes the bromine from the acid, giving a substance melting

at 84—84.5°, which resemble camphoroxalic acid in general properties. The crystals are, however, not identical and will be further examined.

Camphoroxalic acid reacts with benzoic chloride, forming a substance melting at 192—193°, apparently identical with the supposed anhydride produced by the action of acetic anhydride as stated above; with benzoic anhydride, camphoroxalic acid reacts at 150° with evolution of carbonic anhydride, but no definite product could be isolated.

When quickly distilled under ordinary pressure, camphoroxalic acid evolves carbonic anhydride, and some camphor is formed, but the major portion passes over unchanged. Heating with barium hydroxide in a current of dry hydrogen causes hydrolysis to take place at the double linking, with production of barium oxalate and camphor.

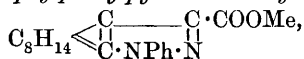
Phenylhydrazine camphoroxalate, prepared by the interaction of the components, separates from alcohol in minute, colourless needles darkening when heated to 205°, and melting and evolving gas at 214—215°; its alcoholic solution gives a red coloration with ferric chloride and a purple with concentrated nitric acid.

When camphoroxalic acid is heated in sealed tubes with dilute sulphuric or hydrochloric acid at 135—150° for several hours, an *acid*, $C_{12}H_{20}O_6$, is formed which crystallises from benzene in clusters of colourless needles melting at 92—93°. It differs from camphoroxalic acid in not yielding any sparingly soluble salts, in not dissolving readily in light petroleum, and in giving a deep blue coloration with alcohol and ferric chloride.

Pure *ethylic camphoroxalate*, prepared by heating the acid with very dilute alcoholic hydrogen chloride, crystallises from light petroleum in fern-like aggregates of long needles melting at 40.5°. It does not form a copper salt, and is miscible with ether in all proportions. With dry ammonia, it gives a sparingly soluble, white *substance*, darkening when heated to 200°, and melting at 225°; with hydroxylamine, a *substance* crystallising from a mixture of toluene and light petroleum in colourless slender needles, melting at 120—121°; with acetic anhydride, acetylcamphoroxalic acid; with bromine, an *additive* compound, which evolves hydrogen bromide, forming a substance resembling the bromocamphoroxalic acid already described. With benzoic chloride or benzoic anhydride, however, no benzoyl derivative could be obtained, thus indicating a greater stability of the ethylic salt than of the free acid.

Methylic camphoroxalate, $C_8H_{14} \begin{smallmatrix} \diagup C \\ | \\ CO \end{smallmatrix} : C(OH) \cdot COOMe$, prepared by the

action of methylic oxalate on camphor, according to instructions given in a previous paper (*loc. cit.*), separates from light petroleum in long, arborescent needles melting at 74.5—75°; it resembles the ethylic salt in general properties. The *phenylhydrazide* forms slender, white needles melting at 204—205°, which, when acted on by glacial acetic acid, give *methylic camphylphenylpyrazolecarboxylate*,



crystallising in colourless needles, and melting at 80.5—81.5°. The

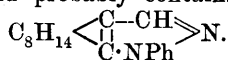
sodium salt is without marked physiological action, whereas the sodium salt of camphoroxalic acid is rapidly toxic.

iso-Amylic camphoroxalate separates in needle-shaped crystals melting at 98·5—99·5°. It gives a sparingly soluble *phenylhydrazide*.

A comparison of the crystallographic characters of camphoroxalic acid and its methylic and isoamylic salts shows that the grade of symmetry of the crystals becomes lower as the molecular weight increases.

The compound obtained by the interaction of phenylhydrazine and camphoroxalic acid is shown to be a phenylhydrazide, as it is readily oxidised with mercuric oxide to give a *substance* crystallising in colourless, monoclinic plates melting at 112°.

When camphyphenylpyrazolecarboxylic acid is distilled with barium hydroxide, a yellowish-green oil passes over, which gives Knorr's pyrazoline reaction, and probably contains camphyphenylpyrazole



A. W. C.

Substances contained in Sesame Oil, and their Relation to the Characteristic Colour Reactions of the Oil. By VITTORIO VILLAVECCHIA and GUIDO FABRIS (*Chem. Centr.*, 1897, ii, 772—773; from *Ann. Lab. chim. centr. delle Gabelle*, 3, 13—26).—Baudouin's colour reaction for sesame oil with hydrochloric acid and cane-sugar is also readily obtained with all those sugars which easily yield furfuraldehyde, and the authors assume this substance to be the cause of the reaction. As a test for sesame oil, they use a 1 per cent. solution of furfuraldehyde in 95 per cent. alcohol with hydrochloric acid, which forms an intense red coloration with the oil. From sesame oil, they have isolated the following substances. (1) *Sesamin*, ($\text{C}_{11}\text{H}_{12}\text{O}_3$)₂, crystallises from alcohol in long, colourless needles, from chloroform in prisms, is insoluble in water, light petroleum, ether, alkalis, and mineral acids, easily soluble in chloroform, benzene, and glacial acetic acid, melts at 123°, has a specific rotatory power $[\alpha]_D = 68\cdot36$ at 22°, does not give the furfuraldehyde reaction, does not combine with iodine, forms neither acetyl nor phenylhydrazine derivatives, and is not attacked by potassium hydroxide, hydrochloric acid, or oxidising agents, but, with nitric acid of sp. gr. = 1·4, yields two crystalline compounds which melt at 235° and 145° respectively. (2) A higher alcohol, $\text{C}_{25}\text{H}_{44}\text{O} + \text{H}_2\text{O}$, which crystallises from alcohol in colourless leaflets having a nacreous lustre, melts at 137·5°, has a specific rotatory power $[\alpha]_D = -34\cdot23$ at 20°, does not give the furfuraldehyde reaction, combines readily with bromine and iodine, yields an acetyl derivative which is a crystalline powder insoluble in water, very easily soluble in benzene, melts at 130—131°, and is easily saponified. (3) A viscous, odourless oil, which is very easily soluble in alcohol, ether, chloroform, and glacial acetic acid, insoluble in water and mineral acids, and very slightly soluble in alkalis. This substance gives the colour reaction with furfuraldehyde and hydrochloric acid.

E. W. W.

Aloins. By EUGÈNE LEGER (*Compt. rend.*, 1897, 125, 185—188).—Analyses of barbaloin made by the author agree best with Groene-wold's formula (*Abstr.*, 1890, 639); it always crystallises with $1\text{H}_2\text{O}$. When treated in pyridine solution with benzoic chloride, it yields an

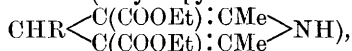
amorphous dibenzoyl derivative, $C_{16}H_{14}Bz_2O_7$, which is readily soluble in alcohol or ether. A diacetyl derivative may be obtained in a similar manner. Barbaloin, partially purified by crystallisation from methylic alcohol, contains another aloin, apparently isomeric with barbaloin, and crystallising from methylic alcohol in yellow, opaque plates containing $3H_2O$. J. J. S.

Aromatic Principles of Capsicum annum, L., and Capsicum fastigiatum, Bl. By JOHANNES MÖRBITZ ((*Chem. Centr.*, 1897, ii, 593; from *Pharm. Zeit. Russ.*, **36**, 299—301, 313—316, 327—331, 341—346, 369—376).—The cayenne fruit contains 0.05—0.07 per cent. of *capsacutin*, $C_{35}H_{54}N_3O_4$, which is obtained by freeing the powdered fruit from fat by means of light petroleum, extracting with ether, hydrolysing the residue left on evaporating the extract, again extracting with ether, evaporating, and finally crystallising the residue from boiling light petroleum. Capsacutin has an extremely pungent taste, which may be detected in a solution containing only 1 part in 11,000,000; it is only slightly soluble in water and light petroleum, but soluble in the ordinary solvents. It is neither a glucoside nor an acid. E. W. W.

2-Methylpyrrolidine. By GOTTFRIED FENNER and JULIUS TAFEL (*Ber.*, 1898, **31**, 906—914).—The 2-methylpyrrolidine prepared from methylpyrrolidone by reduction with amylic alcohol and sodium (Neugebauer and Tafel, *Abstr.*, 1889, 1015) probably contained a little piperidine derived from impurities in the amylic alcohol and the authors have therefore prepared the pure compound by the same method, but using amylic alcohol which had been carefully purified, and have compared the properties of this substance with those of the 2-methylpyrrolidine derived from the 1:2-dimethylpyrrolidine, which is formed by the action of hydrochloric acid on dimethylpiperidine (Merling, *Abstr.*, 1891, 1506; Ladenburg, Mugdan and Brzostowicz, *Abstr.*, 1894, i, 555), the two compounds being found to be in all respects identical. 2-Methylpyrrolidine has a sp. gr. = 0.84 at 20°/20°, and boils at 95.5—96.5° under a pressure of 744 mm. The hydrochloride is very deliquescent, and melts at the temperature of the water bath, whilst the *oxalate* melts at 178—179°; the *platinochloride*, $(C_5H_{12}N)_2PtCl_6$, has no definite melting point, and the *aurochloride*, $C_5H_{12}NAuCl_4$, melts at 158—161°. Dimethylpyrrolidine boils at 96—96.5°, and yields 2-methylpyrrolidine when its hydrochloride is heated in hydrogen chloride. Both methyl- and dimethyl-pyrrolidine are converted by methylic iodide into the methiodide of dimethylpyrrolidine, whilst the corresponding methochloride is formed by molecular change from dimethylpiperidine hydrochloride. *Trimethylpyrrolidineammonium platinochloride* forms yellow, octahedral crystals, and decomposes at 240—250°, whilst the *aurochloride* begins to decompose at 204°. The aurochloride $(C_5H_{12}NCl)_2AuCl_3$, which was formerly ascribed to methylpyrrolidine, is in reality derived from piperidine. A. H.

Condensing Action of Ammonia and Organic Amines in Reactions between Aldehydes and Ethylic Acetoacetate. By EMIL KNOEVENAGEL (*Ber.*, 1898, **31**, 738—748).—The author's conclusions are reproduced below.

I. Nitrogenous products (dihydropyridine derivatives,



are obtained: (1) from an aldehyde, ethylic acetoacetate, and free ammonia; (2) from an aldehyde-ammonia and ethylic acetoacetate (Hantzsch's dihydropyridine synthesis), or from a hydramide [tri-alkyldenediamine, $(\text{R}\cdot\text{CH})_3\text{N}_2$] and ethylic acetoacetate together with ammonia; (3) from an aldehyde and ethylic β -amidocrotonate; (4) from ammonia and a mixture of an ethylic alkyldeneacetoacetate, $\text{CHR}\cdot\text{CAc}\cdot\text{COOEt}$, with ethylic acetoacetate; (5) from an ethylic alkyldeneacetoacetate and β -amido- or a β -monalkylamido-crotonate.

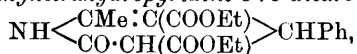
II. Non-nitrogenous products (at low temperatures, ethylic alkyldeneacetoacetates, $\text{CHR}\cdot\text{CAc}\cdot\text{COOEt}$; at higher temperatures, ethylic alkyldenediacetoacetates, $\text{CHR}(\cdot\text{CHAc}\cdot\text{COOEt})_2$, are obtained: (1) from a mixture of an aldehyde and ethylic acetoacetate under the influence of a mon- or di-alkylamine (or of ammonia at a low temperature); (2) from an alkyldenebisdialkylamine, $\text{R}\cdot\text{CH}(\text{NR}_2)_2$, and ethylic acetoacetate; (3) from an aldehyde and an ethylic β -dialkylamidocrotonate; (4) from an ethylic alkyldeneacetoacetate and ethylic acetoacetate, under the influence of alkyl- and dialkyl-amines; (5) from an ethylic alkyldeneacetoacetate and an ethylic β -dialkylamido-crotonate.

It appears that in Hantzsch's dihydropyridine synthesis, the aldehyde-ammonia first reacts with the ethylic acetoacetate to form ethylic ethylideneacetoacetate, ammonia being liberated, and the ammonia converts the second molecule of the acetoacetate into ethylic β -amidocrotonate, which reacts with the ethylideneacetoacetate to form ethylic dihydrocollidinedicarboxylate. All these separate stages can be realised, at any rate to a certain extent. If this view be correct, one of the weightiest arguments in favour of Riedel's pyridine

formula, $\text{CH} \begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{array} \text{N}$, is seriously impaired.

Ethylic β -piperidocrotonate, $\text{C}_5\text{NH}_{10}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$, is described for the first time. It is made by mixing piperidine (1 mol.) with ethylic acetoacetate (1 mol.), removing the oil after 3 hours, drying it over dehydrated sodium sulphate, and distilling it under diminished pressure. It boils at 169° under 15 mm. pressure. C. F. B.

Syntheses in the Pyridine Series. I. An Extension of Hantzsch's Dihydropyridine Synthesis. By EMIL KNOEVENAGEL and A. FRIES (*Ber.*, 1898, 31, 761—767).—When ethylic benzylidenemalonate, $\text{CHPh}\cdot\text{C}(\text{COOEt})_2$ (1 mol.), is heated with ethylic β -amidocrotonate, $\text{NH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$ (1 mol.), for 9 hours at 130 — 150° in a reflux apparatus under 40 mm. pressure, the product is *ethylic 6-oxy-4-phenyl-2-methyltetrahydropyridine-3:5-dicarboxylate*,



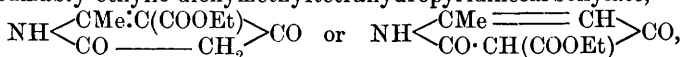
or the corresponding enolic form, and the yield of the crude substance is 75 per cent. of the theoretical. The new compound, which melts at 149.5 — 150° , is hardly soluble in acids or alkalis, and when boiled with strong hydrochloric acid for 10 hours, yields γ -acetyl- β -phenyl-

butyric acid, $\text{CMe} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{COOH}$ (Vorländer, Abstr., 1894, i, 528).

When the heating is continued for 18 hours at $130-150^\circ$, and then for 9 hours at $150-170^\circ$, there is obtained, besides the substance described above, a compound which apparently has the constitution $\text{CMe} \begin{smallmatrix} \text{C}(\text{COOEt}) \cdot \text{CHPh} \\ \text{NH} \text{-----} \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{COOEt}$, and must have been formed by the action of 2 mols. of the amidocrotonate on 1 mol. of the benzilidenemalonate; this compound melts at $179-180^\circ$, and also yields acetylphenylbutyric acid when it is boiled with hydrochloric acid. Two other products, melting at $206-206.5^\circ$ and $262-263^\circ$ respectively, were obtained in addition; these have been shown (following abstract) to be identical with the products of the action of ethylic malonate itself on ethylic β -amidocrotonate.

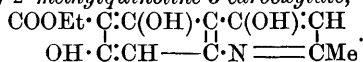
Ethylic ethylidenemalonate reacts in a similar manner to the benzylidene analogue, yielding with ethylic β -amidocrotonate a compound, $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{COOEt}) \\ \text{CO} \cdot \text{CH}(\text{COOEt}) \end{smallmatrix} \text{CHMe}$, which is closely related to the substance obtained by Collie (Trans., 1897, 301, 303; compound A) by heating the hydrochloride of ethylic β -amidocrotonate. C. F. B.

Syntheses in the Pyridine Series. II. Action of Ethylic Malonate on Ethylic β -Amidocrotonate. By EMIL KNOEVENAGEL and A. FRIES (*Ber.*, 1898, 31, 767-776. Compare preceding abstract).—When pure ethylic malonate (1 mol.) is heated with ethylic β -amidocrotonate (1 mol.) and alcoholic sodium ethoxide (1 mol.) for 7-9 hours in a sealed tube at $140-150^\circ$, a product is obtained which is presumably ethylic dioxymethyltetrahydropyridinecarboxylate,



or the enolic form of either of these. It melts at $206-206.5^\circ$, and has both acid and basic properties; its rather unstable *hydrochloride*, with $3\text{H}_2\text{O}$, melts at 152° when heated quickly; further, it yields a *monobromo*-substitution derivative which melts and decomposes at 245° , and also a compound containing very much more bromine (70.5 per cent.); it forms a *dioxime*, which carbonises at $245-255^\circ$; and when boiled with aqueous or alcoholic potash, or strong hydrochloric acid, or when its hydrochloride is heated alone, 4:6-dihydroxy-2-methylpyridine (Collie, Trans., 1891, 617; 1892, 723) is obtained. This substance has feeble basic, but pronounced acid properties; the *potassium* salt crystallises with 1 EtOH.

If the heating be carried out in a reflux apparatus at $130-150^\circ$ under a pressure of 40 mm., 2 mols. of the amidocrotonate appear to react with 1 mol. of the malonate, the product being *ethylic 2:4:4'-trihydroxy-2'-methylquinoline-3-carboxylate*,



This melts at $262-263^\circ$, dissolves in strong hydrochloric acid, but not in alkalis, and loses carbonic anhydride when boiled with alcoholic or aqueous potash, the product, which remains unmelted at 360° , being presumably 2:4:4'-trihydroxy-2'-methylquinoline. C. F. B.

Syntheses in the Pyridine Series. III. Some Acetylpyridines and Acetyldihydropyridines. By EMIL KNOEVENAGEL and WALTER RUSCHHAUPT (*Ber.*, 1898, 31, 1025—1033).—3:5-Diacetyl-4-phenyl-2:6-dimethyl- $\Delta_{2,5}$ -dihydropyridine, $C_5NH_2Me_2PhAc_2$, is obtained by heating benzylideneacetylacetone (Abstr., 1895, i, 50) (1 mol.) with amidoacetylacetone (1 mol.) for 2 hours on a boiling water bath; it is yellow, melts at 180° , and boils at $225\text{--}235^\circ$ under 25 mm. pressure. Dilute nitric acid at $60\text{--}70^\circ$ oxidises the two hydrogen atoms, forming 3:5-diacetyl-4-phenyl-2:6-dimethylpyridine, which melts at 188° .

Ethyllic 3-acetyl-4-phenyl-2:6-dimethyl- $\Delta_{2,5}$ -dihydropyridine-5-carboxylate is obtained by heating either ethylic benzylideneacetoacetate (Abstr., 1896, i, 232) with amidoacetylacetone, or ethylic β -amido-crotonate with benzylideneacetylacetone; it is yellow, melts at 167° , and boils at $210\text{--}230^\circ$ under 25—30 mm. pressure. Dilute nitric acid, at temperatures slightly below 40° , oxidises it to ethylic 3-acetyl-4-phenyl-2:6-dimethylpyridine-5-carboxylate, which melts at $85\text{--}86^\circ$.

Ethylideneacetylacetone, $CHMe:C(CMeO)_2$, was obtained by passing gaseous hydrogen chloride for $\frac{1}{2}$ hour into a dilute chloroform solution of acetaldehyde (1 mol.) and acetylacetone (1 mol.), and then distilling off the chloroform under diminished pressure at 0° ; it boils at 87° , 92° , and 97° under 10, 13, and 18 mm. pressure respectively. When it is mixed with amidoacetylacetone, 3:5-diacetyl-2:4:6-trimethyl- $\Delta_{2,5}$ -dihydropyridine is obtained; this is yellow, melts at 152° , and boils with some decomposition at $220\text{--}230^\circ$ under 20 mm. pressure.

Methylamidoacetylacetone, $NHMe \cdot CMe:CH \cdot CMeO$, prepared by mixing 33 per cent. aqueous methylamine with acetylacetone, melts at 45° , and boils at 200° . When mixed with ethylideneacetylacetone, it forms 3:5-diacetyl-1:2:4:6-tetramethyl- $\Delta_{2,5}$ -dihydropyridine, which is greenish-yellow and melts at 118° .

When diacetyltrimethylidihydropyridine, or ethylic acetyltrimethyldihydropyridinecarboxylate, is boiled for 4 hours with 10 per cent. caustic potash, it is converted into 1:3-dimethyl- Δ_6 -ketotetrahydrobenzene (Hantzsch, Abstr., 1883, 84; Knoevenagel, Abstr., 1895, i, 52):— $NH \begin{smallmatrix} CMe:CAC \\ CMe:CAC \end{smallmatrix} CHMe + 3H_2O = NH_3 + 3CH_3 \cdot COOH +$

$CH \begin{smallmatrix} CMe \cdot CH_2 \\ CO-CH_2 \end{smallmatrix} CHMe.$ Diacetylphenyldimethyldihydropyridine

and ethylic acetylphenyldimethyldihydropyridinecarboxylate are scarcely attacked. With 40 per cent. caustic soda, ethylic acetyltrimethyldihydropyridinecarboxylate yields, in addition to the product mentioned above, a substance which melts at 86° and boils at $155\text{--}160^\circ$ under 15 mm. pressure, and appears to be somewhat impure ethylic trimethyldihydropyridinecarboxylate.

Methylenediacetylacetone (Scholtz, this vol., i, 43) was obtained in crystals incidentally; it melts at 87° . C. F. B.

Action of Concentrated Alkalis on Ethylic Dihydrocollidine-dicarboxylate [2:4:6-Trimethyl- Δ_2 -dihydropyridinedicarboxylate]. By OTTO COHNHEIM (*Ber.*, 1898, 31, 1033—1037).—When this substance is heated with 60—75 per cent. aqueous potash, the

volatile products distill, over at once, more water being added as required; the main product is ethylic trimethyldihydropyridine-carboxylate, which is a solid, melting at 89—90°, and boiling at 140—160° under 15 mm. pressure when still impure, and possessing scarcely any basic properties, unlike the isomeride which Hantzsch obtained, employing hydrochloric acid instead of potash, which was a basic oil. Some 3:5-dimethyl- Δ_2 -ketotetrahydrobenzene (compare preceding abstract) is formed in addition. When an upright tube 60 cm. long is inserted between the flask and the condenser, so that only the more volatile products escape at once from the action of the potash, a small quantity of an oil is obtained which seems to be a mixture of trimethyldihydropyridine with a little trimethylpyridine.

C. F. B.

Action of Formaldehyde on Tetrahydroquinoline. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, 21, 243).—A compound, $\text{CH}(\text{C}_9\text{NH}_{10}\text{Cl})_3$, is formed when a solution of tetrahydroquinoline in concentrated hydrochloric acid is warmed for 10 minutes on the water bath with the requisite quantity of formaldehyde and ferric chloride. It is salted out, filtered, and washed with water, and further purified by solution in alcohol and precipitation with ether. It dyes silk green, and unmordanted cotton a greenish-blue, but not of a sufficiently strong tint to be of use. It is readily soluble in hot water, and with alkalis yields a brown base.

J. J. S.

Action of Tannin and of Gallic Acid on Quinoline Bases. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, 125, 37—38. Compare Abstr., 1897, i, 447, 570).—Pure dry tannin readily dissolves in freshly distilled lepidine, and a red colour is only produced after prolonged exposure to the air and light. Gallic acid reacts in a similar manner, and no difference is observed when solutions of lepidine in absolute alcohol or in dry ether are employed. An aqueous solution of tannin immediately yields a white, curdy precipitate with pure lepidine. Quinoline and quinaldine react in exactly the same manner as lepidine, and in this respect resemble pyridine bases and various volatile alkaloids.

J. J. S.

Amido-2'-hydroxylepidine and Lepidinic Acid. By EMIL BESTHORN and H. BYVANCK (*Ber.*, 1898, 31, 796—804).—When metapenylenediamine (1 mol.) is heated with ethylic acetoacetate (rather more than 1 mol.) in a sealed tube for 5—6 hours up to 130°, *amido-2'-hydroxylepidine* (*amido-2'-hydroxy-4'-methylquinoline*), $[\text{NH}_2 = 2$, or perhaps 4] is formed; it melts at 270°. From metatolylenediamine, *amido-2'-hydroxymethyllepidine* is obtained in a similar manner; it melts above 300°. When the amidohydroxylepidine is boiled with phosphorus oxychloride, a pale yellow *amido-2'-chlorolepidine* is obtained; this melts at 142—143°, and can be converted into 2'-chlorolepidine by first transforming it into the hydrazine hydrochloride, and then boiling the free hydrazine base with copper sulphate in aqueous solution. By diazotising the amidohydroxylepidine and then heating the solution (see also below), pale yellow *hydroxy-2'-chlorolepidine* is obtained; this melts at 214—215°, and is oxidised by alkaline permanganate to

2'-chlorolepidinic acid, which melts and decomposes at 181—182°, crystallises with 2H₂O, and is reduced by boiling with hydriodic acid, potassium iodide, and amorphous phosphorus to lepidinic (4-methylpyridine-5:6-dicarboxylic) acid.

When amido-2'-chlorolepidine is diazotised and the solution heated, *dihydroxylepidine* is formed, in addition to chlorhydroxylepidine; this is also formed when amido-2'-hydroxylepidine is diazotised, and the aqueous solution heated; it decomposes at 270°. Oxidation with alkaline permanganate converts it into *2'-hydroxylepidinic acid*, melting and decomposing at 252—253°, but the yield is poor. C. F. B.

Morpholine Derivatives. By RICHARD STOERMER and MAX FRANKE (*Ber.*, 1898, 31, 752—760; compare *Abstr.*, 1897, i, 473).—1':2'-

Dimethylphenomorpholine, C₆H₄ < $\begin{matrix} \text{O} - \text{CH}_2 \\ \text{NMe} \cdot \text{CHMe} \end{matrix}$, was obtained in the

following manner. 2'-Methylphenomorpholine is allowed to remain for several days with methylic iodide, and the product is made alkaline and extracted with ether. The extract is then freed from ether by distillation, and the residue is benzoylated and shaken with ether and hydrochloric acid, when benzoylmethylphenomorpholine remains dissolved in the ether and the dimethylphenomorpholine in the acid. The latter boils at 259—261°, has an odour like that of naphthalene, and gives a carmine coloration with ferric chloride; the *hydrochloride* melts at 170°, the brownish-yellow unstable *platinochloride* at 144—146° with decomposition (in the presence of excess of platinum tetrachloride, another reddish-white salt, melting at 116° is formed), and the greenish-yellow *picrate* at 136°. By acidifying with hydrochloric acid the alkaline liquid that is left after the extraction with ether described above, evaporating to dryness, extracting the dry residue with absolute alcohol, and precipitating with ether, *trimethylphenomorpholonium iodide*,

C₆H₄ < $\begin{matrix} \text{O} - \text{CH}_2 \\ \text{NMe}_2 \cdot \text{I} \cdot \text{CHMe} \end{matrix}$, melting at 170°, is obtained.

The tertiary base, C₉H₁₃NO₃ or C₉H₁₂NO₃, formed along with methylphenomorpholine when orthonitrophenoxyacetone, in boiling alcoholic solution, is reduced with tin and hydrochloric acid (*loc. cit.*), is now found to contain chlorine, and is shown to be 3-chloro-2'-methylphenomorpholine; for it can be synthesised by boiling the potassium salt of nitrochlorophenol [OH:Cl:NO₂ = 1:3:6] with chloracetone and acetone, and reducing the *chloronitrophenoxyacetone* formed (which melts at 86°, its *semicarbazone* at 195°) in boiling alcoholic solution with tin and hydrochloric acid. Its *hydrochloride* melts at 105—106°, and is readily decomposed by water; the lemon-yellow *nitrosamine* melts at 96·5°, and the *phenylcarbamide*, NHPh·CO·C₈NOH₅MeCl, at 148°.

2-Nitro-1-naphthoxyacetone, NO₂·C₁₀H₆·O·CH₂·COMe, is obtained by heating the potassium salt of 2-nitro-1-naphthol with chloracetone and acetone for 12 hours at 100° in a sealed tube; it is yellowish and melts at 145°; the yellow, unstable *phenylhydrazone* melts at 120°, the yellowish-white *semicarbazone* at 208°, and the *oxime* at 158°. When reduced in boiling alcoholic solution with tin and hydrochloric acid, it yields *methylnaphthamorpholine*, C₁₀H₆ < $\begin{matrix} \text{O} - \text{CH}_2 \\ \text{NH} \cdot \text{CHMe} \end{matrix}$, melting at 95·5°;

the *hydrochloride* melts at 229°, and is readily decomposed by water; the unstable, brownish-yellow *platinochloride* melts at 237°, the lemon-yellow *nitrosamine* (only to be obtained by adding the calculated quantity of amyllic nitrite to an alcoholic solution of the base containing a little hydrochloric acid) at 190°–195° with decomposition, the *phenyl-carbamide* at 180°, and the *acetyl* and *benzoyl* derivatives at 124° and 183·5° respectively.

C. F. B.

Mercury Haloid Compounds of Antipyrine. By M. C. SCHUYTEN (*Chem. Centr.*, 1897, ii, 614–615; from *Bull. Acad. roy. Belg.*, [iii], 33, 821–842).—The mercuric chloride compound, $C_{11}H_{12}N_2O \cdot HgCl_2$, is most soluble in alcohol and water, least soluble in ether, and dissolves in hot benzene, toluene, and carbon bisulphide; the solutions are neutral. When the aqueous solution is evaporated, small, crystalline needles separate, from the other solutions only amorphous residues are obtained. The mercuric bromide compound, $C_{11}H_{12}N_2O \cdot HgBr_2$, is obtained as a white, amorphous precipitate on mixing alcoholic solutions of the two substances; when heated, it melts at 103°, then turns slowly garnet-red, finally charring and giving off fumes of mercuric bromide. It dissolves in alcohol, benzene, and toluene, and is slightly soluble in water, chloroform, ether, and carbon bisulphide.

The mercuric cyanide compound, $C_{11}H_{12}N_2O \cdot HgCy_2$, obtained by mixing hot concentrated aqueous solutions of the components, crystallises in transparent prisms which, on heating, become opalescent at 160–165° and melt at 224°; the yellow, molten mass, on further heating, chars and emits white fumes. The mercury is only incompletely precipitated by sodium peroxide, whilst from the other mercury compounds complete precipitation is effected. According to the author, in these compounds one atom of halogen is directly united to nitrogen, since (1) only one molecule of antipyrine is contained in the compound, whereas other similar mercury haloid compounds usually contain two; (2) with mercurous chloride, antipyrine forms the hydrochloride, mercury, and mercuric oxide; and (3) mercuric iodide, which is not as easily dissociated as the other haloids, does not combine with antipyrine.

E. W. W.

Generalisations as to Melting Points among Pentacyclic Nitrogen Compounds. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 949–953).—The author points out that, just as in the case of substituted malonic acids, so with the phenyl derivatives of tetrazole, the symmetrical compounds melt at relatively higher temperatures than the less symmetrical derivatives.

Malonic acid	134°	Tetrazole	156°
Methylmalonic acid	130	N-(1)-Phenyltetrazole	an oil
Dimethylmalonic acid	180	C-(3)-Phenyltetrazole ...	212–213
Methylisopropylmalonic acid	106–107	Diphenyltetrazole.....	106–107

Another generalisation is that phenyl derivatives of 5-ring nitrogen compounds, in which the phenyl group is attached to nitrogen, melt at a much lower temperature than the isomeric compounds in which the phenyl group is attached to carbon.

Pyrazole	70°	Glyoxalin.....	90°
N-(1)-Phenylpyrazole.....	11	N-Phenylglyoxalin.....	13
C-(3)-Phenylpyrazole	78	N-Phenylpyrroline.....	62
C-(4)-Phenylpyrazole	228	C-Phenylpyrroline	129

The same generalisation applies to alkyl, &c., derivatives.

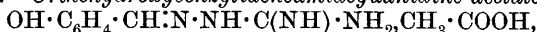
Pyrroline	131°	Glyoxaline	89°
N-(1)-Methylpyrroline	113	N-Methylglyoxaline	- 5
C-(2)-Methylpyrroline (α)	148	C-Methylglyoxaline	137
C-(3)-Methylpyrroline (β)	143		
Triazole	121	Tetrazole	156
C-Methyltriazole.....	94	N-Methyltetrazole	145

The introduction of nitrogen in place of carbon in a cyclic compound tends to raise the melting point.

Pyrroline (1N), liquid; pyrazole (2N), m. p. 70°; glyoxaline (2N), m. p. 89°; triazole (3N), m. p. 121°; tetrazole (4N), m. p. 156°. An exception to this is osotriazole, which melts at 22°, and yet has a very symmetrical formula.

The molecular weights of tetrazole, C-amidotetrazole, and of diphenyltetrazole have been determined, and the numbers indicate that each compound is monomolecular. J. J. S.

Decomposition of 2:5-Diphenyltetrazole into Bladin's N-Phenyltetrazole. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 942—948).—*Orthohydroxybenzylideneamidoguanidine acetate*,



is obtained as follows. Amidoguanidine nitrate (11·2 grams) is dissolved in the least possible quantity of cold water, and the solution then well shaken with salicylaldehyde (10 grams), and finally with concentrated potassium hydroxide, until it has an alkaline reaction; when the odour of the aldehyde has disappeared, the solution is acidified with concentrated acetic acid, and on rubbing the sides of the vessel, the acetate is deposited in the form of a crystalline powder. It is best purified by suspending it in hot benzene and then bringing it into solution by the addition of hot alcohol; at the end of 24 hours, large, colourless crystals are obtained, which, after several recrystallisations, melt at 191—192°. The salt is readily soluble in warm water or alcohol, and sparingly in benzene, acetone, chloroform, or light petroleum; its aqueous solution gives a green coloration with ferric chloride, and with phenyldiazonium chloride it yields a red, gelatinous precipitate melting at 176—177°. This compound, when treated with concentrated nitric acid at 85°, yields an extremely explosive nitro-derivative. 5-Paramidodiphenyltetrazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} : \text{N} \end{smallmatrix}$, is

obtained when the finely powdered nitro-derivative (this vol., i, 336) is reduced with stannous chloride and hydrochloric acid; it is extracted from the alkaline liquid by the aid of chloroform, and purified by repeated recrystallisation from dilute alcohol; it crystallises from ether or dilute acetone in colourless prisms melting at 156°. Its *hydrochloride* crystallises in long, colourless needles, and is practically insoluble in water; the *nitrate*, *acetate*, and *sulphate*, melting at 224—225°, are also described. When diazotised and the diazo-solu-

tion boiled with water, 5-*parahydroxydiphenyltetrazole* is obtained, and, after several recrystallisations from hot water, melts at 190—191°; it crystallises from ether in colourless, glistening needles, is readily soluble in alkalis or warm ammonium hydroxide, dissolves in benzene, alcohol, warm ether, acetone, chloroform, or acetic acid, and is sparingly soluble in warm water, nitric acid, or light petroleum. Bladin's phenyltetrazolecarboxylic acid, $\text{COOH} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N}^{\text{Ph}} \\ \text{N} : \text{N} \end{smallmatrix}$, is obtained when

amidodiphenyltetrazole nitrate is oxidised with potassium permanganate. 2-Phenyltetrazole is obtained when the carboxylic acid is heated in an oil bath at 150—170°. J. J. S.

Action of Diphenyltetrazochloride on Acetoacetic Acid, and on Benzaldehydephenylhydrazone. By EDGAR WEDEKIND [and PAUL BLUMENTHAL] (*Annalen*, 1898, 300, 239—258. Compare Abstr., 1897, i, 443).—*Cycloformazyl methyl ketone*, $\text{COMe} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \\ \text{N} = \text{N} \cdot \text{C}_6\text{H}_4 \end{smallmatrix}$,

prepared by the action of diphenyltetrazochloride on acetoacetic acid, is a brownish-red, amorphous powder without definite melting point. The *phenylhydrazone*, which crystallises from a mixture of chloroform and petroleum, melts at about 205—210°; it is insoluble in alkali, and the solution in concentrated sulphuric acid is brownish-red. Phenylhydrazine also yields another compound, which melts at 197°, and dissolves in alkali; it forms a carmine-red solution in concentrated sulphuric acid.

Paraphenylformazylbenzene (formazyl-diphenyl),
 $\text{NHPh} \cdot \text{N} : \text{CPh} \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{Ph}$,

obtained by the action of diphenyltetrazochloride on benzaldehydephenylhydrazone under the influence of alcoholic potash, is a greenish-violet, crystalline powder with bronze reflex, and melts at 174°. The solution in concentrated sulphuric acid is red, and becomes yellowish-brown when heated.

Paraphenylhydroxyazobenzene, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{Ph}$, is produced on adding an alcoholic solution of diphenyltetrazochloride to a solution of phenol in caustic potash; the solution in concentrated sulphuric acid is carmine-red. It begins to sinter at about 240°.

Diformazylbenzene, $\text{C}_{12}\text{H}_8(\text{N} : \text{N} \cdot \text{CPh} : \text{N} \cdot \text{NHPh})_2$, prepared by the action of diphenyltetrazochloride on the phenylhydrazone of benzoylformic acid, crystallises from dilute alcohol in needles, and melts at 153°. Oxidation converts it into *bistriphenyltetrazolium hydroxide*, which sinters at 260—278°, remaining solid at 285°; alkaline reducing agents regenerate diformazylbenzene. M. O. F.

Derivatives of Cinchonine. By EDOUARD GRIMAU (Compt. rend., 1898, 126, 575—578).—The bromomeroquinine hydrobromide, $\text{C}_9\text{H}_{14}\text{BrNO}_2 + \text{HBr}$, obtained by Kœnigs by the action of bromine on the crude product of the oxidation of cinchonine and quinine, loses only one atom of bromine when treated with silver nitrate at the ordinary temperature. When treated with picric acid or potassium picrate, it yields the salt $\text{C}_9\text{H}_{14}\text{BrNO}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3 \cdot \text{OH}$, which crystallises in yellow lamellae melting at 203—204°, and is only slightly soluble in

cold water. The nitroso-derivative, $C_9H_{13}BrNO_2 \cdot NO$, obtained by the action of nitrous acid on the hydrobromide, forms nacreous crystals which melt at $87.5-88^\circ$. When the hydrobromide is heated with concentrated aqueous potash, it yields nacreous plates of the compound $C_9H_{14}BrNO_2 + KBr$.

By heating the hydrobromide with water and zinc powder, impure meroquinene is obtained, and this yields an acetyl derivative, $C_9H_{14}NO_2Ac$, which forms small, white crystals melting at 112.5° .

Hydroxymeroquinene is obtained by the action of excess of silver hydroxide on the hydrobromide; it crystallises from a mixture of methylic alcohol and ether in small, white crystals insoluble in ether and chloroform, but very soluble in water and methylic and ethylic alcohols. It decomposes without melting, and its solutions have an alkaline reaction.

C. H. B.

Yohimbehe Bark and Yohimbine. By HERMANN THOMS (*Chem. Centr.*, 1897, ii, 978-979; from *Ber. pharm. Ges.*, 7, 279-283).—From a sample of bark named Yumbehoa, the author obtained 0.54 per cent. of a mixture of two alkaloids, from which Spiegel's yohimbine (*Chem. Zeit.*, 1896) was separated by means of benzene. The other alkaloid forms a green fluorescent solution in chloroform, but could not be obtained in a crystalline state. According to Prof. Schumann, this bark is almost certainly identical with yohimbehe bark. The leaves of the Yumbehoa tree also contain yohimbine.

E. W. W.

An Oxyptomaine. By WILLIAM OESCHNER DE CONINCK (*Compt. rend.*, 1898, 126, 651-653).—The ptomaine, $C_8H_{11}N$ (Abstr. 1888, 730 and 1118), when treated with very dilute hydrogen peroxide in the dark, yields an oxyptomaine, $C_8H_{11}NO$, together with yellowish, resinous products. The oxyptomaine is a non-deliquescent, white solid, which softens at 250° , melts at a slightly higher temperature, and decomposes suddenly at about 260° . It dissolves readily in acids, and forms a crystallisable hydrochloride, $C_8H_{11}NO \cdot HCl$, and a corresponding platinochloride, both of which are gradually decomposed when boiled with water.

When heated with zinc powder, the oxyptomaine yields the original base, $C_8H_{11}N$ which is a collidine, and hence the oxy-derivative may be called *collidone*. It is the higher homologue of the oxy-pyridines previously described.

C. H. B.

A New Enzyme—Caroubinase. By JEAN EFFRONT (*Compt. rend.*, 1897, 125, 116-118).—The carbohydrate caroubin (this vol., i, 398) is readily hydrolysed by dilute acid, and also by a special diastase, *caroubinase*, which is produced during the fermentation of the seeds; the secretion of the enzyme is somewhat slow during the actual period of fermentation, and increases with the formation of chlorophyll. Alcohol precipitates the active principle from infusions of the growing germs. Caroubinase acts energetically at 40° , its maximum activity being at about $45-50^\circ$, but becoming very feeble at 70° , and the enzyme is completely destroyed at 80° . An addition of 0.01-0.03 per cent. of formic acid increases the hydrolytic power of the enzyme. The sugar obtained by the hydrolysis of caroubin with this enzyme is not identical with that formed under the influence of dilute acids.

J. J. S.

Peptone Salts from Glutin. By CARL PAAL (*Ber.*, 1898, 31, 956—966. Compare Abstr., 1892, 895).—The author has made further experiments with three peptone hydrochlorides of different composition obtained from glutin. The peptone salt (20 grams), dissolved in 5 times its weight of water, was dialysed during 3 days into a litre of water, which was renewed daily; the contents of the dialyser and of the outer vessel were then separately evaporated in platinum vessels, and the residues dried by heating their methylic or ethylic alcoholic solutions in a vacuum. About 12 grams of one salt was found to have diffused; this portion was readily soluble in ethylic alcohol, whereas the salt which had not diffused was practically insoluble in ethylic alcohol but dissolved readily in cold methylic alcohol. The two salts also differed materially in their composition and also in molecular weight.

The author has succeeded in isolating the substances which are not precipitated when the peptone salts are treated with phosphotungstic acid; these were obtained in the form of a thick syrup, and were partially precipitated by alcohol, and completely by ether, in yellowish lumps. The dried substance gave 6.26 per cent. of ash, which consisted entirely of lime obtained from the barium hydroxide used. The substance gave a strong biuret reaction.

Glutin peptone barium (Ba = 9.25 per cent.) and ferropeptone were obtained from the peptone contained in the phosphotungstic acid precipitate. When the peptone salt is boiled with absolute ethylic alcohol and saturated with hydrogen chloride, a salt is obtained containing a rather higher percentage of hydrogen chloride, probably brought about by the water produced during etherification, as it has already been shown that peptone hydrochlorides are fairly readily etherified.
J. J. S.

Crystallisation of Animal Proteids. By F. GOWLAND HOPKINS and STANISLAW N. PINKUS (*J. Physiol.*, 1898, 23, 130—136).—If an equal bulk of saturated solution of ammonium sulphate is added to white of egg, the fixed alkali of the proteid liberates ammonia, and this interferes with the separation of crystals; if, however, this is neutralised with acetic acid, the process of crystallisation is much accelerated; and still more is this the case if a slight excess of the acid is added. Evaporation is then unnecessary to obtain crystals, and there can be no confusion between them and crystals of ammonium sulphate; their affinity for carbol-magenta or methylene blue is also distinctive, should any confusion arise. Analogous results were obtained with serum albumin.
W. D. H.

Action of Superheated Water on Proteid. By RICHARD NEUMEISTER (*Zeit. Biol.*, 1898, 36, 420—424).—The points of difference between Salkowski (this vol., ii, 173) and the author are explained as being chiefly due to the former's imperfect acquaintance with the published work of the latter.
W. D. H.

Organic Chemistry.

Mixed Fluorine and Bromine Derivatives Containing Two Atoms of Carbon. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1897, ii, 1098—1099; from *Bull. Acad. roy. Belg.*, [iii], 34, 307—326. Compare *ibid.*, 33, 439—474).—When a mixture of 200 grams of difluorotetrabromethane with 34 grams of antimony trifluoride and 20 grams of bromine is heated for 30 hours at 130° in a platinum apparatus, *difluorotribromethane*, $\text{CBr}_2\text{F}\cdot\text{CHBrF}$, and a small quantity of *trifluorodibromethane*, $\text{CBrF}_2\cdot\text{CHBrF}$, are formed; the latter is a rather volatile, colourless liquid with an odour like that of carbon tetrachloride, is not affected by light, and boils at 81.5° . The former is a colourless liquid which turns yellow under the influence of light, has a pleasant odour, is insoluble in water, does not attack glass, becomes turbid when exposed to moist air, does not burn, boils at 146° , has a sp. gr. = 2.60772 at 17.5° , 2.60277 at 20° , and a specific refractive index = 1.50787 at 17.5° . When a cooled alcoholic solution is reduced with zinc-dust and the evolved vapours collected in alcohol at -10° or -25° , *difluorobromomethylene*, $\text{CBrF}\cdot\text{CHF}$, is obtained as a colourless, limpid, and extremely volatile liquid which is not affected by light, boils at 19.6° under 770 mm. pressure, has a sp. gr. = 1.84337 at 0° and a specific refractive index = 1.3846 at 0° . It combines very energetically with bromine, forming difluorotribromethane, and oxidises slowly to an acid which contains fluorine, and is very deliquescent. When sodium ethoxide acts on difluorotribromethane, *difluorodibromomethylene*, $\text{CBrF}\cdot\text{CBrF}$, is formed with considerable rise of temperature; this is a colourless liquid, has an unpleasant odour, is not affected by light, boils at 70.5° under 771 mm. pressure, has a sp. gr. = 2.31212 at 20° , and a specific refractive index = 1.45345 at 20° . It combines readily with oxygen with considerable liberation of heat, forming *fluorodibromacetic fluoride*, $\text{CBr}_2\text{F}\cdot\text{COF}$, from which *fluorodibromacetic acid*, $\text{CBr}_2\text{F}\cdot\text{COOH}$, may be obtained by the action of water. The *sodium* salt of this acid is deliquescent, very soluble in water, and soluble in alcohol; the *barium* salt is crystalline, deliquescent, and soluble in alcohol, and the *amide* crystallises in white needles, is slightly soluble in water and easily so in ether. *Ethyllic fluorodibromacetate*, prepared by the action of water and alcohol on fluorodibromacetic fluoride, is a liquid with the odour of peppermint. Difluorodibromomethylene does not undergo polymerisation; when it is dissolved in chloroform and treated with bromine, *difluorotetrabromethane*, $\text{CBr}_2\text{F}\cdot\text{CBr}_2\text{F}$, is formed; this is a white, volatile, crystalline substance, has a strong odour of camphor, is easily soluble in alcohol, soluble in acetic acid, melts at 62.5° , and boils at 186.5° under 758 mm. pressure.

By the replacement of bromine by fluorine in an unsaturated compound, the boiling point is lowered constantly by about 10° ; in

saturated compounds, the boiling point is also lowered. In some cases, the replacement of hydrogen by fluorine increases the stability of the molecule, thus tetrabromomethane cannot be distilled under the ordinary pressure, whilst fluorotetrabromomethane, under these conditions, is only slightly decomposed, and difluorotetrabromomethane requires to be heated to a temperature very much above the boiling point before it decomposes.

E. W. W.

Specific Gravity of Iodoform. By F. BEYERINCK (*Chem. Zeit.*, 1897, 21, 853).—Recrystallised iodoform has sp. gr. = 4.008 at 17°. Saturated solutions of iodoform in bromoform have a specific gravity = 2.97, and are useful in mineral separations.

J. J. S.

Alkylis Isocyanurates; Formula and Constitution of Cyanuric Acid. By PAUL LEMOULT (*Compt. rend.*, 1897, 125, 869—871).—Methylic isocyanurate, $C_3N_3O_3Me_3$, prepared by Wurtz's method, crystallises in voluminous crystals melting at 175°. The author confirms Wurtz's statement that the ethylic salt melts at 95°; Limpricht and Habich found it to melt at 85°.

The following thermochemical data have been obtained.

	Molecular heat of combustion.		Heat of formation.
	(1) At constant volume.	(2) At constant pressure.	
Methylic salt ...	704.22 Cal.	703.8 Cal.	172.5 Cal.
Ethylic „ ...	1167.83 „	1168.27 „	197.9 „

The differences between the heats of combustion of the two salts at constant pressure (3×154.8) indicates that they are true homologues. The difference, however, between the methylic salt and free cyanuric acid (compare Abstr., 1896, ii, 11) shows that the methyl groups in the salt cannot be attached to carbon, but agrees better with the supposition that they are attached to nitrogen.

The constitution of the acid is then $CO \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{NH}$, a formula which agrees with the decomposition of the acid into carbonic anhydride and ammonia under the influence of alkalis.

J. J. S.

Action of Alkylis Haloids on Mercaptides. By KARL A. HOFMANN and W. O. RABE (*Zeit. anorg. Chem.*, 1898, 17, 26—34. See also Abstr., 1897, i, 310).—*Mercury mercaptiodide*, $HgI \cdot S \cdot Et$, obtained by cautiously warming mercury mercaptide with ethylic iodide, crystallises in slender, pale yellow needles, and is not decomposed when boiled for an hour with water or alcohol. When treated with concentrated sulphuric acid, either cold or hot, no iodine or hydrogen iodide is liberated; with boiling sodium hydroxide, it is converted into an orange-coloured compound which contains mercaptan and mercury, but no halogen; and with concentrated potassium cyanide, it yields mercury cyanide and mercaptan. It is also obtained by the action of mercaptan on an alcoholic solution of mercury iodide, and by mixing alcoholic solutions of mercury mercaptide and mercury iodide.

When the mixture of mercury mercaptide and ethylic iodide is

heated for some time at 80—100°, an oily mixture of the double compounds, $\text{HgI}_2\cdot\text{SEt}_3\text{I}$ and $\text{HgI}_2\cdot 2\text{SEt}_3\text{I}$, is obtained. They are separated by crystallisation from acetone, in which, at ordinary temperatures, the former compound only is soluble; this melts at 107·5° and has been described in a previous paper. The compound, $\text{HgI}_2\cdot 2\text{SEt}_3\text{I}$, obtained alone when mercury mercaptide with excess of ethylic iodide is heated under pressure for 80 hours at 75°, separates from alcohol or acetone in white crystals, and melts at 147°.

The action of ethylic bromide on mercury mercaptide takes place in a manner analogous to that of ethylic iodide. *Mercury mercaptobromide*, $\text{HgBr}\cdot\text{SEt}$ is obtained at the ordinary temperature, or better by warming the mixture at 40—50°; it crystallises from alcohol in colourless tablets, turns yellow at 190°, and sinters at 202—203°. The compound, $\text{HgBr}_2\cdot\text{SEt}_3\text{Br}$, obtained together with the following compound by heating the mixture under pressure for 48 hours at 75°, and separated by prolonged fractional crystallisation from acetone and methylic alcohol, crystallises in thin, lustrous plates belonging to the monosymmetric system, and melts at 104°. The compound $\text{HgBr}_2\cdot 2\text{SEt}_3\text{Br}$ was not obtained free from the preceding compound; it melts at 139—145°.

Mercury mercaptonitrate, $\text{NO}_3\cdot\text{Hg}\cdot\text{SEt}$, obtained by leading nitric oxide, prepared from sodium nitrite and fuming nitric acid, through an alcoholic solution of mercury mercaptide, is a white powder insoluble in water, alcohol, and all ordinary solvents; it carbonises when heated, with the formation of a mercury mirror. When it is dissolved in hydrochloric acid, mercaptan is evolved; it yields a clear solution in cold, concentrated sulphuric acid, which, on heating, yields mercuric sulphate and nitrogen peroxide, and reacts with sodium hydroxide and potassium cyanide in a manner analogous to the mercury mercaptohaloids. It is also obtained by mixing solutions of mercury nitrite and mercury mercaptide and as an intermediate product in the oxidation of mercury mercaptide with concentrated nitric acid.

The compound $(\text{HgBr}\cdot\text{SEt})_2\cdot\text{NH}_3$, obtained by treating mercury mercaptobromide suspended in absolute alcohol or ether with dry ammonia, is a white, amorphous powder, turns yellow when gently heated, and carbonises at a higher temperature with the formation of a mercury mirror; it yields ammonia when treated with sodium hydroxide, and mercaptan when treated with hydrochloric acid.

The compound $\text{HgNO}_3\text{SEt}\cdot\text{NH}_3$, is obtained from mercury mercaptonitrate in a similar manner to the preceding compound, which it closely resembles in properties, except that it crystallises in lustrous plates.

Mercury mercaptoiodide does not combine with ammonia, even when heated at 100° with concentrated ammonia under pressure; this is not surprising when one remembers the instability of the ammonia compounds with mercuric iodide.

E. C. R.

Action of Phosphoric Acid on Glycerol. By ADRIAN and AUGUSTE TRILLAT (*J. Pharm.*, 1898, [vi], 7, 226—230).—Glycerophosphoric acid, obtained by decomposing its barium salt with sulphuric

acid, invariably contains a large proportion of barium hydrogen glycerophosphate; attempts to obtain the pure acid by decomposing the potassium salt with tartaric acid, and the lead and copper salts by hydrogen sulphide, failed on account of the simultaneous formation, in the former case of potassium hydrogen glycerophosphate, and in the latter of phosphoric acid. When glycerophosphoric acid is liberated from its barium salt by a slight excess of sulphuric acid, and the solution concentrated, either by boiling or by slow evaporation, gradual decomposition takes place, glycerol and phosphoric acid being formed.

When the proportions given by Portes and Prunier (*J. Pharm.*, 1894, 393) for preparing calcium glycerophosphate are employed, a limit of the action, corresponding with a limit of etherification, occurs when 21 per cent. of glycerophosphoric acid has been produced. In addition to the latter, there appears to be formed a *diglycerophosphoric acid*, $\text{H}(\text{C}_3\text{H}_7\text{O}_2)_2\text{PO}_4$, which is neutral to methyl-orange, but becomes strongly acid when boiled with alcohol or water, owing to the formation of glycerophosphoric and phosphoric acids. W. A. D.

Caroubinose. By JEAN EFFRONT (*Compt. rend.*, 1897, 125, 309—311).—Caroubinose, the sugar obtained by the hydrolysis of caroubin with mineral acids (this vol., i, 398), is a non-crystallisable syrup, soluble in alcohol or water, and having the composition $\text{C}_6\text{H}_{12}\text{O}_6$. It differs from *d*-glucose in its rotatory power, which is $[\alpha]_D = 24$. When caroubin is not completely hydrolysed to caroubinose, an intermediate, white, amorphous substance is obtained; this is insoluble in 95 per cent. alcohol, but dissolves in water, and is non-fermentable. When caroubinose is treated in the usual manner with phenylhydrazine hydrochloride and sodium acetate, a mixture of a phenylhydrazone and an osazone is obtained. The *phenylhydrazone*, $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_5$, forms pale yellow prisms which sink to the bottom of the liquid; it is best purified by washing with boiling absolute alcohol, which removes any osazone, and then successively with cold water, alcohol, and ether; it is soluble in boiling dilute alcohol, but undergoes partial decomposition at the same time; it has a definite melting point, namely, 183° . The *osazone*, $\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_4$, can only be obtained free from the phenylhydrazone by repeated recrystallisation; it melts at 198° , crystallises in yellow needles, and is sparingly soluble in water or in cold alcohol, but dissolves readily in hot alcohol.

J. J. S.

Chemistry of Starch. By CARL J. LINTNER (*Chem. Zeit.*, 1897, 21, 737—738 and 752—754).—The author points out the necessity of distinguishing between ordinary inversion dextrins, reversion dextrins, vegetable gums which are anhydrides of pentoses, and the products obtained by Zulkowski on heating starch with glycerol. All these groups of compounds are often spoken of as dextrins, but differ materially in their more important properties. General directions for the isolation of dextrins are given, and the paper concludes with an account of amylopectin, erythropectin, achropectin and isomaltose.

J. J. S.

Action of Diastase on Starch. By HANS MITTELMEIER (*Chem. Centr.*, 1897, ii, 1010—1011; from *Mon. sci.*, [iv], 11, 2, 775—776. Compare Abstr., 1896, i, 336).—According to the author, the first stage of the action of diastase on starch results in the formation of equal amounts of two different amyloextrins, of which one is much more easily attacked by diastase than the other. Thus, while the one has only arrived at the erythroextrin stage, the other has passed through all the stages from dextrin to sugar. On this hypothesis, the existence of a molecule of sugar and a molecule of dextrin in one molecular complex is intelligible. The author has prepared gelatinous osazones, and isolated an osazone which is apparently derived from an isomeride of maltose. E. W. W.

Gum-ammoniacum. By M. FRISCHMUTH (*Chem. Centr.*, 1897, ii, 1078; from *Pharm. Zeit. Russ.*, 36, 555—559).—The gum has the properties of a true carbohydrate, or, at least, contains true carbohydrate groups, the average rotatory power of the gum being -32.825° , which is not affected by any acid or alkaline reaction of the liquid. When treated with hydrochloric acid of 20 per cent., it yields, besides humus matters, levulinic acid, and on oxidising with nitric acid of sp. gr. = 1.15, it yields 31.3 per cent. of its weight of mucic acid (equivalent to 41.75 per cent. of galactose), but no saccharic acid. When distilled with dilute hydrochloric acid, it yields 9.35 per cent. of furfuraldehyde (equivalent to 16.67 per cent. of arabinose), and when boiled with dilute (1.25 per cent.) sulphuric acid, reducing sugars are obtained consisting chiefly of galactose. No cellulose could be detected. L. DE K.

Synthesis of Organic Compounds by means of the Dark Electric Discharge. By ALEXANDER DE HEMPTINNE (*Chem. Centr.*, 1897, ii, 1044—1045; from *Bull. Acad. roy. Belg.*, [iii], 34, 269—277).—The author finds that when mixtures of various gases are submitted to the action of the electric discharge in a Berthelot's ozoniser, the best results are usually obtained when the walls of the apparatus are near together; for each mixture, a certain definite distance is probably most advantageous. In the case of carbonic oxide and water vapour, the author has confirmed Losanitsch and Jovitschitsch's results (Abstr., 1897, i, 179); when the discharge passed through a distance of 7 mm. for 3 hours, the pressure was only reduced by 15 mm. of water, and only a little carbonic anhydride and formic acid were produced. With carbonic oxide and hydrogen, however, increasing the distance traversed by the discharge has apparently little effect on the formation of formaldehyde and its polymerides. Carbonic oxide and methane yield an aldehyde-like compound, and carbonic oxide and ethane, when cooled, form a ketone and a considerable quantity of aldehyde; both syntheses take place most readily when the walls of the ozoniser are not far apart. When a mixture of ethylic alcohol and oxygen is similarly treated, the best yield of acetic acid is obtained when the lower part of the apparatus is immersed in a freezing mixture, so that the acid which collects is solidified, and thus removed from the sphere of action. E. W. W.

Aldehyde-ammonia. By MARCEL DELÉPINE (*Compt. rend.*, 1897, 125, 951—954).—*Ethylideneimine*, CHMe:NH or $(\text{CHMe:NH})_3$, obtained when aldehyde-ammonia is placed in a vacuum over sulphuric acid for several days, crystallises in brilliant, colourless crystals, melts at about 85° , boils at 123 — 124° under atmospheric pressure, has an odour resembling that of acetamide, and is soluble in water, alcohol, acetic acid, chloroform, benzene, or toluene; when its chloroform or benzene solution is allowed to evaporate spontaneously, the imine is obtained in the form of large, transparent crystals, resembling those of potassium bromide. Its molecular weight in benzene solution varies inversely with the concentration. Its vapour density at 261° agrees with the simple formula CHMe:NH , but at lower temperatures the vapour density is higher.

Heat of combustion at constant volume = 347.13 Cal.

" " " " pressure = 347.6 "

" formation for $(\text{CH}_3\text{CHNH})_3$ = 40.5 "

Determinations of the molecular weight of aldehyde-ammonia point to the formula $(\text{C}_2\text{H}_7\text{NO})_3$. The vapour density at 182° indicates that decomposition into water and the simple imine has taken place.

Heat of combustion at constant volume = 346.54 Cal.

" " " " pressure = 347.0 "

$\text{C}_2 + \text{H}_7 + \text{N} + \text{O} = \text{C}_2\text{H}_7\text{NO}$ cryst. + 83.1 Cal.

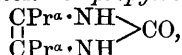
$\text{C}_2 + \text{H}_5 + \text{N} + \text{H}_2\text{O}$ liq. = $\text{C}_2\text{H}_7\text{NO}$ cryst. + 14.1 Cal.

The *picrate* of ethylideneimine is obtained when a saturated alcoholic solution of picric acid is added to an alcoholic solution of either aldehyde-ammonia or ethylideneimine; it crystallises in long, bright yellow needles, and is extremely readily soluble in water, but the solution readily decomposes into aldehyde and ammonium picrate.

J. J. S.

The Butyroids and Isovaleroin. By AUG. BASSE and HEINRICH KLINGER (*Ber.*, 1898, 31, 1217—1225. Compare Abstr., 1891, 890).—The results of the following investigation confirm the view previously entertained by Klinger and Schmitz as to the constitution of the products obtained by the action of sodium on acid chlorides. This reaction does not appear to be a direct one, but is brought about by the presence of a small amount of water, the reduction being effected by the hydrogen liberated from this, and from the hydrogen chloride which is produced. Butyroid, as already described, is converted by aqueous potash into dipropylglycollic acid, melting at 78° , and yields an osazone, $\text{N}_2\text{HPh:CPra:CPra:N}_2\text{HPh}$, which melts at 138° , and reacts in a similar manner to benzoin with carbamide and thiocarbamide.

4:5-Dipropylglyoxaline 2-hydrosulphide, $\begin{array}{c} \text{CPra}\cdot\text{NH} \\ | \\ \text{CPra}-\text{N} \end{array} \rangle \text{C}\cdot\text{SH}$, obtained from thiocarbamide, crystallises in long, yellowish needles which do not melt below 290° . It has faintly acid properties, but its potassium salt is decomposed by water. Dipropylacetylenemono-ureide,



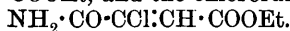
which is obtained from carbamide, crystallises in silky needles, which melt and decompose at 216° .

Isobutyroin, $\text{COPr}^{\beta}\cdot\text{CHPr}^{\beta}\cdot\text{OH}$, is prepared in a similar manner to the normal compound, and boils at $75-77^{\circ}$ under a pressure of 12 mm. 4:5-*Di-isopropylglyoxaline 2-hydrosulphide* crystallises in hard, white needles, which do not melt below 290° , whilst the corresponding *di-isopropylacetylenemono-ureide* closely resembles it.

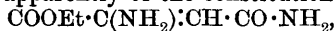
Isovaleroïn boils at $80-105^{\circ}$ under a pressure of 13 mm., and is converted by phenylhydrazine into *di-isovalerylosazone*, $\text{C}_{22}\text{H}_{30}\text{N}_4$, which crystallises in slender needles melting at 163° . 4:5-*Di-isobutylglyoxaline 2-hydrosulphide* crystallises in small, white needles, and is soluble in alkalis. *Di-isobutylacetylenemono-ureide* crystallises in slender, silky needles melting at $182-183^{\circ}$. *Isovaleroïnoxime*, $\text{C}_4\text{H}_9\cdot\text{C}(\text{NOH})\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{OH}$, forms lustrous plates melting at 128° . When isovaleroïn is heated with aqueous potash in a current of air, it is partially converted into *di-isobutylglycollic acid*, which crystallises in soft needles melting at $119.5-120^{\circ}$. A. H.

Some Constituents of Wool Fat. By ERNST SCHULZE (*Ber.*, 1898, 31, 1200—1202).—In view of the results obtained by Darmstädter and Lifschütz (this vol., i, 245) the author points out that he has confirmed the formula previously ascribed by him to ischolesterol, and further draws attention to the great variation which exists in the composition of different wool fats. A. H.

Constitution of Amidofumaric and Amidomaleic Derivatives. By RENE THOMAS-MAMERT (*Bull. Soc. Chim.*, 1897, [iii], 17, 60—66).—Potassium amidofumaramate, obtained by treating amidofumaramide with the calculated amount of potassium hydroxide, may be either $\text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{NH}_2)\cdot\text{CH}\cdot\text{COOK}$ or $\text{COOK}\cdot\text{C}(\text{NH}_2)\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, but as, on reduction with aluminium amalgam in neutral solution, the potassium salt of isoasparagine, $\text{NH}_2\cdot\text{CO}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{COOH}$, and not that of the normal compound, $\text{COOH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CONH}_2$, is obtained, the former formula must be adopted. The isoasparagine was identified by means of its copper salt, and was also separated in the free state. Since the ethylic amidofumaramate melting at 139.5° , obtained by the action of alcoholic ammonia on ethylic chlorofumaramate, also yields isoasparagine, it must be represented by the formula $\text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{NH}_2)\cdot\text{CH}\cdot\text{COOEt}$, and the chlorofumaramate by



The compound melting at 119.5° , isomeric with ethylic amidofumaramate, obtained by treating ethylic amidofumamate with aqueous ammonia, and thus apparently of the constitution



yields, however, isoasparagine on reduction, and since it differs considerably in its properties from the fumaric derivatives described, it is probably the stereoisomeric ethylic amidomaleamate. Attempts were made to determine the constitution of potassium ethylic amidofumamate by ascertaining which of the two ethylaspartic acids it yielded on reduction, but hydrolysis always occurred at some stage of the process, and inactive aspartic acid was obtained. Considering,

however, that ammonia is without action on the salt, and that in ethylic amidofumarate only the ethoxyl-group in the vicinity of the amido-group is attacked by ammonia, it appears most probable that potassium ethylic fumaramate is $\text{COOK} \cdot \text{C}(\text{NH}_2) : \text{CH} \cdot \text{COOEt}$.

N. L.

The Tautomeric Forms of the Ethereal Salts of α -Ketonic Acids. By ROBERT SCHIFF (*Ber.*, 1898, 31, 1304—1306. Compare this vol., i, 355).—Since such salts are obtained by the condensing action of sodium ethoxide, they might be expected to have the enolic form, but it has not yet been possible to obtain the ketonic form. There is indirect evidence that they contain the group $\text{C}(\text{OH}) \cdot \text{COOEt}$; for not only do they give, in benzene solution, colorations with ethereal ferric chloride, but they resemble lactic acid, which also contains this group, in that they form compounds containing the group $\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CH} \cdot \text{CCl}_3$, when they are heated with excess of chloral hydrate at 100° or 150° .

Acetylpyruvic chloralide, $\text{CHAc} : \text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CH} \cdot \text{CCl}_3$, melts at 137 — 138° ; *benzoylpyruvic chloranilide* at 197 — 198° .

A sample of ethylic acetoacetate manufactured by the Höchst Colour Works, has been found to consist entirely of the enolic form, like the sample from Kahlbaum's described previously.

C. F. B.

Organic Urates Soluble in Water. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, 21, 544).—The urates of the following bases are soluble in hot water; namely, methylamine, benzylamine, nicotine, tetrahydroisoquinoline, and piperazine. The urates of piperidine, ethylamine, and propylamine are readily soluble in cold water.

J. J. S.

Constitution of Inorganic Compounds. XIV. Molecular Compounds of Tin Tetrahaloids with Tin Alkyls. By ALFRED WERNER and PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1898, 17, 82—110).—Tindiethyl di-iodide was prepared according to Cahour's method, by heating ethylic iodide with tin foil in a sealed tube for 20 hours at 150° ; it is most easily separated from the tintriethyl iodide, which is also formed, by dissolving it in methylic alcohol and precipitating with a small quantity of water. A determination of the molecular weight by Beckmann's boiling point method gave numbers agreeing with the formula SnEt_2I_2 . Tindiethyl salts are most easily prepared from tindiethyl oxide, which is obtained by treating the iodide dissolved in alcohol with ammonia, is a white powder, and when treated with acids is converted into the corresponding salts. The chloride crystallises from light petroleum in silky needles, and melts at 84 — 85° . The bromide crystallises from light petroleum in prisms or tablets and melts at 63° . The sulphate crystallises from water in beautiful, quadratic crystals, does not melt when heated, and is not volatile with steam; the molecular weight determination gave numbers corresponding to half that required by the formula SnEt_2SO_4 . The *phosphate*, $\text{SnEt}_2\text{PO}_4\text{H}$, crystallises from water in large, white

needles; it is soluble in water, and at first yields a clear solution, which, however, quickly becomes turbid and deposits a white powder containing phosphoric acid. Tindiethyl salts, when treated with ammonium carbonate, yield a white precipitate soluble in excess of ammonium carbonate, which is again precipitated by the addition of acid. With ammonium sulphide, a white precipitate is also obtained soluble in excess and again precipitated by hydrochloric acid. With hydrogen sulphide, a heavy oil is precipitated which has not been examined. According to the authors, compounds of the formula SnX_2Et_2 are capable of existing in stereoisomeric forms, and from stereochemical grounds tindiethyl sulphate can only exist in the *cis*-form, but the halogen compounds are probably of the *trans*-form, as this is the most stable; when, however, the sulphate is treated with barium iodide, the product is ordinary tindiethyl iodide. Tindiethyl salts are capable of forming molecular compounds only with ammonia and its substitution derivatives.

Tindiethyl chloride pyridine, $\text{SnEt}_2\text{Cl}_2 \cdot 2\text{C}_5\text{NH}_5$, formed with evolution of heat when its constituents are mixed, crystallises from pyridine in transparent prisms, melts at 130° , gradually loses pyridine when exposed to the air, and may be crystallised without decomposition from absolute alcohol and light petroleum. The *bromide* crystallises in prisms or rhombic tablets and melts at 140° with decomposition. The *iodide* crystallises in white prisms, melts at 117° , is easily soluble in alcohol, and is much more readily decomposed than the chloride or bromide.

Tindiethyl chloride and iodide do not yield definite compounds with aniline; according to the length of time of the action of the aniline, the crystalline product varies in composition between the compounds $\text{SnEt}_2\text{X}_2 \cdot \text{NH}_2\text{Ph}$ and $\text{SnEt}_2\text{X}_2 \cdot 2\text{NH}_2\text{Ph}$.

Tindiethyl chloride diammine, $\text{SnEt}_2\text{Cl}_2 \cdot 2\text{NH}_3$, obtained by treating a solution of tindiethyl chloride in absolute ether with dry ammonia, is an amorphous, white powder insoluble in all the ordinary solvents and decomposes when heated, and when treated with water or potassium hydroxide. The *iodide*, $\text{SnEt}_2\text{I}_2 \cdot 2\text{NH}_3$, is very similar to the chloride and gradually becomes yellow after a time.

Tintriethyl iodide and tintetrethyl are prepared according to Ladenburg's method, by the action of ethylic iodide on an alloy of tin and sodium containing 14 per cent. of sodium. The mixed product is separated by fractional distillation and the tintetrethyl finally separated from the small quantity of tintriethyl iodide, which it always contains, by dissolving it in absolute ether and treating the solution with dry ammonia, whereby the insoluble compound, $\text{SnEt}_3\text{I} \cdot 2\text{NH}_3$, is precipitated and the tintetrethyl is removed from the filtrate by distillation. Three molecular compounds of tintriethyl iodide are already known, namely $\text{SnEt}_3\text{I} \cdot 2\text{NH}_3$, $\text{SnEt}_3\text{I} \cdot 2\text{NH}_3 \cdot \text{C}_5\text{H}_{11}$, and $\text{SnEt}_3\text{I} \cdot 2\text{NH}_2\text{Ph}$. The authors have examined the last compound, and find that it remains unaltered when crystallised either from aniline or alcohol, and therefore it contains the maximum number of aniline molecules; it crystallises in lustrous, white leaflets, and melts at 58° . The authors were unable to obtain a compound of tintriethyl

iodide with pyridine. Compounds with piperidine and dipropylamine are easily formed, but have not been examined.

Tintetrethyl does not form additive compounds; although the authors experimented with a large series of oxides, sulphides, and nitrides. Tintetraphenyl is also incapable of forming additive compounds; it is soluble in many organic bases and sulphides, and crystallises from all of them unchanged.

Leadtetraphenyl, prepared by the action of bromobenzene on lead sodium alloy, is separated from the diphenyl by treatment with alcohol, in which the diphenyl is easily soluble. It does not form additive compounds, and crystallises unchanged from dipropylamine and diethylic sulphide. When dissolved in chloroform and treated with a current of dry hydrogen chloride, it yields leaddiphenyl chloride.

Tin tetrachloride bisdimethylic sulphide, $\text{SnCl}_4 \cdot 2\text{SMe}_2$, is obtained by the action of methyl sulphide on anhydrous tin chloride, the reaction being so violent that it is necessary to cool the mixture; it is a white, crystalline mass, very sparingly soluble in methylic sulphide, is decomposed at once by water, and gradually decomposes when allowed to remain even in a closed vessel. The *ethyl* compound, $\text{SnCl}_4 \cdot 2\text{SEt}_2$, obtained in a similar manner to the preceding compound, crystallises from ethylic sulphide in large, white prisms, melts and decomposes at $101\text{--}102^\circ$, is easily soluble in alcohol and ether, and is decomposed by water with the formation of ethylic sulphide. The *amyl* compound, $\text{SnCl}_4 \cdot 2\text{S}(\text{C}_5\text{H}_{11})_2$, is a white, crystalline mass, and melts and decomposes at 64° .

Tin tetrabromide bisdimethylic sulphide, $\text{SnBr}_4 \cdot 2\text{SMe}_2$, is obtained as a crystalline mass and melts at $85\text{--}87^\circ$. It is remarkable for its intense yellow colour, although both its components are colourless; and as the colour is completely destroyed when it is decomposed by water, it is apparently characteristic of the compound, and is not due to decomposition products. The two following compounds have the same colour. The *ethyl* compound, $\text{SnBr}_4 \cdot 2\text{SEt}_2$, crystallises from ethylic sulphide in large, transparent prisms, melts at 84° , is easily soluble in alcohol and ether, and is decomposed by water with the formation of ethylic sulphide. The *amyl* compound, $\text{SnBr}_4 \cdot 2\text{S}(\text{C}_5\text{H}_{11})_2$, melts at $45\text{--}46^\circ$.

Tin tetrachloride pyridine, $\text{SnCl}_4 \cdot 2\text{C}_5\text{NH}_5$, is formed from its components with evolution of a large amount of heat and forms an amorphous, white powder, which is insoluble in all the ordinary solvents; when heated it decomposes without melting and loses pyridine when boiled with methylic alcohol. The *tetrabromide pyridine*, $\text{SnBr}_4 \cdot 2\text{C}_5\text{NH}_5$, is a white, amorphous mass resembling the tetrachloride, and decomposes on exposure to the air. The compounds of tin tetrachloride and tindiethyl chloride with pyridine both contain 2 molecules of pyridine to 1 molecule of tin haloid.

Although tin tetrahaloids form additive compounds with sulphides and pyridine, when treated with alcohols the additive compound is decomposed as soon as formed, hydrogen haloid is evolved, and compounds of the composition $\text{SnCl}_3 \cdot \text{OEt}, \text{EtOH}$ are formed. When tin tetrachloride and absolute alcohol, both cooled to -10° , are mixed, a

white, crystalline powder is obtained. The compounds from tin tetrabromide and ethylic alcohol or amylic alcohol are similar.

E. C. R.

Furfurylsuccinic Acid. By S. S. SANDELIN (*Ber.*, 1898, 31, 1119—1122).—Ethylic furfurylidenemalonate, $C_4OH_3 \cdot CH:C(COOEt)_2$ (Marckwald, *Abstr.*, 1888, 678), was converted into furfurylsuccinic acid by the method of Bredt and Kallen (*Abstr.*, 1897, i, 154). The furfurylidenemalonate (1 mol.) in alcoholic solution was treated with potassium cyanide (2 mols.) in aqueous solution, the mixture boiled for 6 hours in a reflux apparatus, and the alcohol distilled off. It was not found possible to isolate pure cyano- β -furfurylpropionic acid, $C_4OH_3 \cdot CH(CN) \cdot CH_2 \cdot COOH$, from the residue; this residue was heated with aqueous potash until ammonia was no longer evolved, after which the solution was acidified, and the furfurylsuccinic acid extracted with ether.

Furfurylsuccinic acid, $C_4OH_3 \cdot CH(COOH) \cdot CH_2 \cdot COOH$, melts and decomposes at 154° ; the *ethylic* salt boils at 199.5 — 200° under 79 mm. pressure, the *methylic* salt at 162 — 163° under 33 mm.; the *anil* melts at 152.5° . When the acid is heated under 67 mm. pressure, it evolves gas at 145° , and at 196 — 210° a substance distills which is nearly all β -furfurylpropionic acid, $C_4OH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$ (Baeyer, *Abstr.*, 1877, 444), no anhydride being formed, as is the case with phenylsuccinic acid (Bredt and Kallen, *loc. cit.*). C. F. B.

Phenylic Iododichloride. By FERD. KEPPLER (*Ber.*, 1898, 31, 1136—1137).—Phenylic iododichloride, $C_6H_5 \cdot ICl_2$, cannot be kept in sealed tubes, even in the dark; it decomposes, forming parachloriodobenzene and hydrogen chloride. It remains unchanged, at any rate for two months, when it is placed in the bottom of an open desiccator with a dish of sulphuric acid over it, and the whole is kept in a dark place. C. F. B.

Formation of Acetylquinol from Acetaldehyde and Quinone in Sunlight. By HEINRICH KLINGER and WILHELM KOLVENBACH (*Ber.*, 1898, 31, 1214—1216. Compare *Abstr.*, 1891, 900).—Acetaldehyde slowly combines with benzoquinone when exposed to sunlight, acetylquinol, $C_6H_3Ac(OH)_2$, being formed, which is identical with that described by Nencki and Schmid (*J. pr. Chem.*, 1881, 23, 547). The *monacetate*, $OAc \cdot C_6H_3Ac \cdot OH$, crystallises in broad, yellowish needles melting at 91° , and the *phenylhydrazone* of this compound crystallises in almost colourless needles and melts at 147° . The *diacetate* also forms needles and melts at 68° , whilst the *dibenzoate* crystallises in prisms melting at 113° , and yields a *phenylhydrazone* which crystallises in straw-coloured needles and melts at 148° .

A. H.

Oxide of Dichloromethoxyquinonedibenzoylmethylacetal. By C. LORING JACKSON and H. A. TORREY (*Amer. Chem. J.*, 1898, 20, 395—430. Compare *Abstr.*, 1897, i, 272).—When the oxide of dichloromethoxyquinonedibenzoylmethylacetal, previously called dichlorodimethoxyquinol dibenzoate, is treated with sodium hydroxide, it is

converted into sodium chloranilate; with sodium methoxide, it gives dichlorodimethoxyquinonedimethylhemiacetal.

Sodium methoxide acts on the ethyl oxide in a similar manner, the ethoxy-groups being replaced by methoxy-groups; the converse also being true, that when the methyl oxide is acted on by sodium ethoxide the methoxy- are replaced by ethoxy-groups.

Isoamylamine acts on the methyl oxide, giving an unstable, yellow substance, which, when heated, passes into the *isoamylamine salt of dichlorisoamylamidoxyquinone*, $C_5H_{11}\cdot NH\cdot C_6Cl_2O_2\cdot NH_2(OH)\cdot C_5H_{11}$; this crystallises from a mixture of benzene and methylic alcohol in purplish-red needles, and when heated decomposes into isoamylamine and *dichlorisoamylamidoxyquinone*; the latter can also be obtained by the action of hydrochloric acid on any of its salts; it forms bronze-black, flattened needles or long plates melting at 188° . The *silver salt* forms olive-grey needles containing $2H_2O$, which are lost on heating to 110° , the substance becoming red; and the barium *salt* consists of violet, crystalline plates.

Dichlorodi-isoamylamidoquinone, $(C_5H_{11}NH)_2C_6Cl_2O_2$, obtained by the action of isoamylamine on chloranil, or dichlorodimethoxyquinone, or dichlorodimethoxyquinonedimethyldibenzoylacetel, crystallises in long, dark red plates or flattened needles, often showing a marked purple iridescence when separating from solution, and melts at $224-225^\circ$.

Isoamylamine chloranilate, prepared by the action of the amine on chloranilic acid, is a purplish-red, crystalline substance. Di-isoamylamine acts on the oxide, giving rise to the *di-isoamylamine salt of dichlorodidi-isoamylamidoxyquinone*, which separates from light petroleum in reddish-brown crystals melting at $168-169^\circ$.

Dichlorodidi-isoamylamidoquinone, $C_6Cl_2O_2[N(C_5H_{11})_2]_2$, produced by the action of di-isoamylamine on chloranil, crystallises from alcohol in long, reddish-black needles; it is very unstable, readily giving off di-isoamylamine, and no accurate melting point could be taken.

Hydroxylamine is without action on the oxide, but phenylhydrazine gives a yellow substance, not further investigated.

Dichlorodimethoxyquinonedimethyldiacetylacetel, prepared by the action of acetic chloride on the sodium salt of dichlorodimethoxyquinonedimethylhemiacetal, crystallises from a mixture of chloroform and alcohol in white, monoclinic prisms or rhombic plates melting at $177-178^\circ$. When heated with sulphuric acid, only chloranilic acid could be isolated, and not an oxide similar to the one obtained from the benzoylacetel. The corresponding *diethyl* derivative crystallises in very sharp, rhombic plates with bevelled edges, and melts at $120-121^\circ$.

With the hope of ascertaining whether the atom of oxygen in the oxide is in the ortho- or meta-position, the authors have studied the action of sulphuric acid on certain dihydric phenols. Without obtaining any definite evidence, they believe it has the ortho-attachment.

Tetrabromoguaiacol, $OMe\cdot C_6Br_4\cdot OH$, obtained by the action of bromine on guaiacol, crystallises from chloroform in long, white, slender prisms or thick needles melting at $162-163^\circ$. When treated

with concentrated nitric acid in glacial acetic acid solution, a red substance is formed, probably tetrabromorthoquinone.

Tribromoveratrole, $C_6HBr_3(OMe)_2$, prepared by the action of methylic iodide on tribromoguaiacol, crystallises from hot alcohol in slender, white needles melting at $86-87^\circ$. With concentrated nitric acid, it also yields a red substance, probably tribromorthoquinone.

The action of sodium alkyl oxides on some substituted quinones was begun by the authors, but given up on account of Astre's work (Abstr., 1896, i, 18, 153) in a similar direction; they cannot, however, agree with Astre's formulæ for the substances produced, in which sodium is supposed to have replaced hydrogen attached to the benzene ring.

When sodium chloranilate is treated with iodine and sodium hydroxide, iodoform is produced. A. W. C.

Action of Acetic Anhydride on Quinone and on Dibenzoylstyrene. By JOHANNES THIELE (*Ber.*, 1898, 31, 1247—1249).—When quinone (150 grams) is added in small quantities to acetic anhydride (400—450 grams) containing concentrated sulphuric acid (10 c.c.), it rapidly dissolves, and the liquid becomes hot; after maintaining the temperature at $40-50^\circ$ until all the quinone is added, the solution is poured into much water, when the triacetyl derivative of hydroxyquinol separates; this melts at $96.5-97^\circ$, and is identical with the compound described by Barth and Schreder; the yield obtained by this method represents 80 per cent. of that required by theory. The substance forms a colourless solution in concentrated sulphuric acid, dilution with a small quantity of water developing a pink coloration, which is destroyed on further addition of the diluent. The acetate distils considerably above 300° without undergoing decomposition; it is very readily hydrolysed by acids and alkalis.

Acetyltriphenylfurfuranol, $\begin{matrix} C(OAc):CPh \\ | \\ CPh=CPh \end{matrix} > O$, is obtained by suspending dibenzoylcinnamene, $CPh \cdot C(COPh):CH(COPh)$, in acetic anhydride, and treating it with a small quantity of concentrated sulphuric acid; it crystallises from alcohol in long, lustrous prisms, and melts at 135° . A minute quantity of the substance develops a beautiful, bright green fluorescence with concentrated sulphuric acid.

A mixture of acetic anhydride and concentrated sulphuric acid converts the two naphthaquinones into the same triacetyl derivative of 1:2:4-trihydroxynaphthalene; terephthalaldehyde yields the tetracetyl derivative, $C_6H_4[CH(OAc)_2]_2$. M. O. F.

Characteristic Reaction of Orthophenols: Derivatives of Antimonyl catechol. By HENRI CAUSSE (*Compt. rend.*, 1897, 125, 954—956). Compare Abstr., 1893, i, 75).—The property, which all orthophenols possess, of forming antimonyl derivatives, similar to those previously described in the case of catechol and pyrogallol, serves as the basis of a method for separating them from their isomerides. Certain other phenols also form somewhat similar derivatives, but the latter are amorphous, are readily dissociated by cold alcohol, and do not yield halogen derivatives, &c. The best method of separating

the antimonyl derivatives is by the aid of dilute halogen hydracids; the derivative of the ortho-compound crystallises out, and all other derivatives are decomposed.

Antimonylcatechol chloride, $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} SbCl$, is best obtained by the action of an aqueous solution of antimony chloride on catechol; it often contains a quantity of the hydroxy-compound, from which it can be freed by solution in hydrochloric acid, diluting, and then boiling; when cold, the chloride crystallises in plates which are insoluble in the usual solvents.

The *bromide*, $C_6H_4O_2SbBr$, may be obtained in a similar manner, or more readily by dissolving the hydroxide in hydrobromic acid.

The *iodide* is best obtained by diluting 50 c.c. of a 50 per cent. solution of hydriodic acid with 3—4 times its volume of water, saturating with potassium iodide, then with oxide of antimony, and finally adding 25 grams of catechol; the solution is then poured into a solution of catechol (25 grams) in water (50 grams), previously heated to 40—50°, when the iodide crystallises out.

The *fluoride*, $C_6H_4O_2SbF$, and *oxalate*, $C_6H_4O_2Sb \cdot C_2HO_4$, are also described; the latter is best obtained by adding a hydrochloric acid solution of the chloride to a boiling solution of potassium hydrogen oxalate.

J. J. S.

Composition of Wool Fat, VI. The Cholesterols of Wool Fat. By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1898, 31, 1122—1127. Compare this vol., i, 245).—When the half-liquid Fraction 2, obtained in the separation of the alcohols of the soft fat by means of methylic alcohol, is dissolved in 2—3 volumes of ether and allowed to remain at 0°, small, white needles of a substance, Alcohol 2a, separate; these melt at 76—77°, and solidify at 70—72°. When the ether is evaporated from the filtrate and the residue is diluted largely with light petroleum, flakes remain undissolved; these dry to a resinous substance, designated Alcohol 2b. The filtrate from this, after evaporation of the petroleum, leaves a neutral, yellow, viscid liquid free from inorganic constituents: Alcohol 2c.

When a small quantity of Alcohol 2c is dissolved in glacial acetic acid, and a little strong sulphuric acid is added, the solution turns pale reddish-yellow, without becoming hot, and then becomes green, when its absorption spectrum shows a pronounced narrow band between C and d, and a less pronounced one at D. Neither cholesterol nor isocholesterol behave like this. If, however, the solution is diluted with an equal volume of acetic anhydride, it becomes warm, and after an hour the absorption bands of cholestol and isocholesterol can be observed. When the alcohol is heated with 2—3 parts of benzoic anhydride on the water bath, it yields an amorphous, soft, buttery benzoate, soluble in acetic acid; from this, the alcohol can be regenerated by hydrolysis with alcoholic potash. In addition, a mixture of two crystalline benzoates, insoluble in acetic acid, is obtained; this yields, when hydrolysed, a mixture of about 2 parts of cholesterol with 1 of isocholesterol. Probably Alcohol 2c is a sort of hydrated cholesterol. Cholesterol

can be converted into it, to the extent of 20—25 per cent., by boiling with alcoholic potash of double normal strength.

When a solution of ischolesterol in acetic anhydride is heated to boiling with a drop of strong sulphuric acid, the solution turns green, and shows the absorption bands of cholesterol. If the boiling is continued until the solution has acquired a permanent violet-red tint, and the cooled solution is diluted with absolute alcohol, the green, alcoholic solution shows the bands of both ischolesterol and cholesterol, and the small, insoluble residue gives Liebermann's cholestol reaction with acetic anhydride and a drop of sulphuric acid, just as cholesterol does.

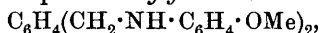
The following amounts of different substances have been obtained from 100 parts of the alcohols of the soft fat: Alcohol 2c, 50—54; ischolesterol, 11; Alcohol 2a, 3—4; Alcohol 2b, 6—7; non-cholesterols, not yet investigated, 24—30. C. F. B.

Chemical Activity of Organic Ammonium Salts. By JULIUS TAFEL (*Ber.*, 1898, 31, 1152—1154).—The following experiments were undertaken to investigate the action of reagents on certain groups, when present in an ion of an electrolyte, and for this purpose the quaternary ammonium salts were chosen. Phenyltrimethylammonium hydrochloride and hydrobromide are not acted on in aqueous solution by chlorine or bromine, which are not electrolytes. The salts of aniline, on the other hand, and those of methylaniline and dimethylaniline, are readily converted into halogen derivatives in this way, and this may be due to the fact that the salts of these bases readily dissociate in solution into the free base and acid. Phenyltrimethylammonium nitrate, however, is readily converted by nitric acid, which is an electrolyte, into *mononitrophenyltrimethylammonium nitrate*, which crystallises in long, yellow prisms. Triethylallylammonium bromide combines very readily with bromine in aqueous solution to form a *perbromide*, which loses bromine on exposure to the air, yielding *triethyldibromopropylammonium tribromide*, $C_3H_5Br_2 \cdot NEt_3Br_3$, crystallising in colourless, silky plates. When the solution of this substance in acetone is heated, bromine is removed, with formation of *triethyldibromopropylammonium bromide*, $C_3H_5Br_2 \cdot NEt_3Br$, which crystallises in colourless, silky plates. A. H.

Action of Orthoxylylenic Bromide on Primary Aromatic Amines. By MAX SCHOLTZ (*Ber.*, 1898, 31, 1154—1158. Compare this vol., i, 305, 383).—When heated with orthoxylylenic bromide, orthochloraniline yields *xylylenebisorthochloraniline*,



which crystallises in colourless plates melting at 79° ; whilst the corresponding *xylylenebisorthobromaniline* crystallises in white plates melting at 132° . Orthanisidine and α -naphthylamine only react with one bromine atom of the dibromide in chloroform solution in the cold, but when the substances are heated together in alcoholic solution, complete reaction takes place. *Xylylenebisorthanisidine*,



crystallises in long, delicate needles melting at 105° , whilst *xylylene-*

bis-α-naphthylamine melts at 148°. *β-Naphthylamine*, on the other hand, yields 2'-*β-naphthylidihydroisindole*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} N \cdot C_{10}H_7$, which crystallises in colourless plates melting at 232°. This shows that the second ring of the naphthalene molecule acts in the same way as a group in the ortho-position to the amido-group. The presence of two ortho-groups appears to hinder the reaction more powerfully than a single group, for mesidine, $C_6H_2Me_3 \cdot NH_2$ [$Me_3 : NH_2 = 1 : 3 : 5 : 6$], does not yield any compound analogous to those formed by ortho-amines; whilst the isomeric pseudocumidine [$Me_3 : NH_2 = 1 : 3 : 4 : 6$] undergoes the normal reaction. Orthomethylbenzylamine, $C_6H_4Me \cdot CH_2 \cdot NH_2$, in which the amido-group is not combined with a carbon atom of the ring, acts like a meta- or para-compound, and yields *orthomethylbenzylidihydroisindole*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} N \cdot CH_2 \cdot C_6H_4Me$, which has not been obtained in the solid form, but yields a crystalline *hydrochloride*.
A. H.

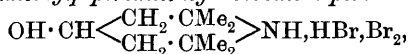
Some Perhaloids. By A. SAMTLEBEN (*Ber.*, 1898, 31, 1141—1148).—A number of perhaloid compounds, NR_2R' , HX , X_2 , have been prepared by adding either a hydrochloric acid solution of iodine chloride, bromine, or a solution of iodine in potassium iodide to a solution of a salt of a mixed aliphatic-aromatic tertiary amine at 0°. With the exception of the periodides, these compounds are decomposed by water, and still more readily by alkalis, periodo- or parabromo-derivatives being formed; should the para- (or even, in the case of dimethyl- and diethyl-toluidine, the ortho-) position be occupied, either the original amine is regenerated, or resinous products are formed. The numbers quoted below are melting (or decomposing) points.

Dimethylaniline hydrochloride chloriodide, NMe_2Ph, HCl, ICl , yellow, 77°. *Diethylaniline hydrochloride chloriodide*, an oil; *periododiethylaniline*, 32°. *Parabromodimethylaniline hydrochloride chloriodide*, $C_6H_4Br \cdot NMe_2, HCl, ICl$, yellow, 113°. *Tetramethyldiamidobenzophenone hydrochloride chloriodide*, $CO(C_6H_4 \cdot NMe_2, HCl, ICl)_2$, yellow, 76°. *Nitroso-dimethylaniline hydrochloride chloriodide*, $NO \cdot C_6H_4 \cdot NMe_2, HCl, ICl$, yellow, 164°. *Diethylaniline hydrobromide perbromide*, NEt_2Ph, HBr, Br_2 , orange-red, 81°. *Diethylorthotoluidine hydriodide periodide*,

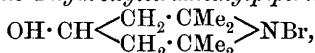
$C_6H_4Me \cdot NEt_2, HI, I_2$, steel-blue to dark brown, 100°. *Parabromodimethylaniline hydriodide periodide*, brownish-red, 124—125°.

Phenyltrimethylammonium iodide and iodine chloride yield a mixture of phenyltrimethylammonium periodide, NMe_3PhI, I_2 , and *chloride-chloriodide*, NMe_3PhCl, ICl , yellow, 118°.

4-Hydroxytetramethylpiperidine hydrobromide perbromide,



red, 160°, yields *bromo-4-hydroxytetramethylpiperidine*,



yellow, 101°, when it is treated with aqueous alkalis. The latter

substance is also obtained by the action of bromine on the free base.
 1 : 2 : 2 : 6 : 6-*Pentamethylpiperidine hydrobromide perbromide*, 145°.

C. F. B.

Reaction of Diazo-salts with Phenols. By CHARLES GASSMANN and HENRY GEORGE (*Compt. rend.*, 1897, 125, 306—309).—The authors have come to the conclusion that all phenols and naphthols, which, when united with a diazo-salt, yield orthohydroxy-derivatives, can react with such diazo-salts in neutral or even acid solutions. Several examples are given.

A 15 per cent. solution of β -naphthol in triacetin is recommended as a reagent suitable for titrating diazo-solutions; it is preferable to the usual reagent, namely, sodium 2-naphthol-3 : 3'-disulphonate.

It has been noticed that, as a rule, nitrated diazo-salts react with phenols more readily than do simple diazo-salts. Two different dyes may be obtained from orthonitrobenzidine by diazotising, and then combining it with salicylic acid and 1-naphthol-4-sulphonic acid; the product varies according to the order in which the latter reagents are employed. The constitution of these two dyes is explained by the generalisation regarding nitrated derivatives given above.

J. J. S.

Halogenised Diazonium Thiocyanates, and their Rearrangement into Thiocyanodiazonium Salts. By BENNO HIRSCH (*Ber.*, 1898, 31, 1253—1268. Compare Hantzsch and Hirsch, *Abstr.*, 1896, i, 428).—*Parabromobenzenediazonium thiocyanate* is prepared from parabromobenzenediazonium chloride and potassium thiocyanate in absolute alcohol at 0°, and separates, on adding absolute ether, in the form of a reddish resin, which becomes yellow and solid when rubbed with a glass rod; it is sparingly soluble in absolute alcohol, but is very hygroscopic, and when freshly prepared dissolves readily in water.

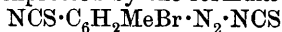
Parathiocyanobenzenediazonium bromide, $\text{NCS} \cdot \text{C}_6\text{H}_4 \cdot \text{NBr} : \text{N}$, is obtained on extracting the foregoing compound with spirit, and filtering into common ether; it is more conveniently prepared by allowing the ice-cold solution of freshly-prepared parabromobenzenediazonium chloride to remain at the ordinary temperature for 8—10 minutes after filtration from the potassium chloride, when ether precipitates the thiocyanodiazonium salt. Free hydrochloric acid also exerts a favourable influence in the rearrangement of parabromobenzenediazonium thiocyanate. The compound obtained in the manner described is almost white, those diazonium bromides which have been hitherto prepared being intensely yellow; it dissolves with some difficulty in ordinary alcohol, and remains unchanged in the desiccator. It explodes with great violence at about 94°.

Orthochlorobenzenediazonium thiocyanate is a dark yellow compound which explodes at 46°. *Orthothiocyanobenzenediazonium chloride* explodes at 105°.

Metachlorobenzenediazonium thiocyanate forms yellow needles, and explodes with great violence in air; when preserved in a desiccator of brown glass, it quickly disappears, filling the vessel with vapour.

It has not been converted into metathiocyanobenzenediazonium chloride.

3 : 5-Dibromoparatoluenediazonium thiocyanate, $[\text{Me} : \text{Br}_2 = 1 : 3 : 5]$, is an orange, crystalline substance, which decomposes without explosion at $40-50^\circ$. It yields two products of rearrangement, which probably have the composition expressed by the formulæ



and $\text{NCS} \cdot \text{C}_6\text{H}_2\text{MeBr} \cdot \text{N}_2 \cdot \text{Br}$ respectively.

Trithiocyanobenzenediazonium thiocyanate, $(\text{NCS})_3\text{C}_6\text{H}_2 \cdot \text{N}_2 \cdot \text{NCS}$, is prepared by treating tribromobenzenediazonium sulphate with excess of potassium thiocyanate, tribromobenzenediazonium thiocyanate (*loc. cit.*) being produced when the calculated quantity is employed; it is an intensely yellow, amorphous substance, inexplosive at ordinary temperatures, and detonating at $79-80^\circ$. It is very sparingly soluble in water, and, after a long interval, develops a blood-red coloration with a dilute solution of ferric chloride. Boiling water liberates hydrothiocyanic acid, whilst cold acetone and aniline eliminate nitrogen; when the latter substance is employed, detonation occurs.

M. O. F.

Rearrangement of Benzylidenephénylhydrazone. By JOHANNES THIELE and ROBERT H. PICKARD (*Ber.*, 1898, 31, 1249—1251).— β -Benzylidenephénylhydrazone is obtained when the ordinary phenylhydrazone of benzaldehyde, suspended in 4 parts of acetic anhydride, is cooled with ice and treated with a further quantity of the anhydride containing a small proportion of zinc chloride or concentrated sulphuric acid; when dissolution is complete, water is added, and the colourless product crystallised from a small quantity of glacial acetic acid; it forms small, white needles, and melts at 136° .

The new phenylhydrazone is readily soluble in organic solvents excepting petroleum, and dissolves more freely than the α -compound. It is very labile, changing completely into the isomeride when exposed in the desiccator during about a week; the same alteration takes place in a few hours when the substance is heated in a toluene bath, and in a still shorter period (30 minutes) when the solution in alcohol is treated with a few drops of alcoholic potash.

β -Benzylidenephénylhydrazone gives Bülow's reaction, and yields the dibenzylidenediphenylhydrotetrazone obtained from α -benzylidenephénylhydrazone and amylic nitrite (compare *Abstr.*, 1895, i, 74); it does not, however, give rise to the compound (m. p. 202°) isolated by Ingle and Mann (*Trans.*, 1895, 606). With iodine in presence of sodium ethoxide, it yields exclusively *syn*-benzileosazone, whilst α -benzylidenephénylhydrazone gives rise to dibenzylidenedihydrotetrazone along with this product. When lead peroxide is added to a solution of the α -phenylhydrazone in glacial acetic acid, dibenzylidenedihydrotetrazone is precipitated, a portion of the phenylhydrazone remaining dissolved; the β -compound, however, gives no precipitate, but on adding water and extracting the product with benzene, alcohol precipitates a small quantity of *anti*-benzileosazone.

In view of the behaviour of the two modifications of benzylidene-

phenylhydrazone, the authors regard them as stereoisomerides, representing the α -compound by the formula $\text{C}_6\text{H}_5 \cdot \begin{array}{c} \text{CH} \\ || \\ \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5 \end{array}$, its relation to the β -compound being indicated by the expression $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \\ || \\ \text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{N} \end{array}$, for the latter substance.

Benzophenonephenylhydrazone and the phenylhydrazone of phenyl paratolyl ketone are indifferent to the action of acetic anhydride containing concentrated sulphuric acid. M. O. F.

Bromination of Alkylated Phthalimides: Derivatives of Methylphthalimide. By FRANZ SACHS (*Ber.*, 1898, 31, 1225—1233).—The most convenient method of preparing alkyl derivatives of phthalimide is by distilling the phthalate of the corresponding amine; this process giving more satisfactory results than treatment of potassium phthalimide with an alkyl iodide. Determinations in which the thermometer thread was completely surrounded with the vapour of the boiling substance show that the methyl, ethyl, propyl, isopropyl, and butyl derivatives of phthalimide boil at 285.7° (761 mm.), 285.0° (758 mm.), 296.9° (758 mm.), 286.0° (761 mm.), and 311.8° (758 mm.) respectively.

Bromomethylphthalimide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \cdot \text{CH}_2\text{Br}$, obtained by the action of bromine on methylphthalimide at 160 — 170° during 5—8 hours, crystallises from chloroform or benzene in rhombic prisms, and melts at 149 — 150° . The substance produces an irritating effect on the mucous membrane. When heated with hydrobromic acid, it yields phthalic acid, ammonium bromide, and formaldehyde.

Methoxymethylphthalimide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \cdot \text{CH}_2 \cdot \text{OMe}$, prepared by heating a solution of bromomethylphthalimide in methylic alcohol with finely powdered potassium cyanide, crystallises from hot alcohol in colourless needles, and melts at 120 — 121° . *Ethoxymethylphthalimide* formed on heating bromomethylphthalimide dissolved in absolute alcohol with potassium iodide, and also produced when an attempt is made to recrystallise crude bromomethylphthalimide from alcohol, crystallises from petroleum or benzene in long needles, and melts at 83° , boiling at 325° (corr.) under atmospheric pressure.

Hydroxymethylphthalimide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \cdot \text{CH}_2 \cdot \text{OH}$, is obtained when bromomethylphthalimide is dissolved in boiling water, from which it separates in crystals containing water of crystallisation; when recrystallised from toluene, it melts at 141 — 142° , decomposing at 184° with elimination of formaldehyde; it has a feeble, bitter taste. The *hydriodide* crystallises from chloroform in large, robust, monoclinic prisms, and melts at 148 — 150° ; it is insoluble in warm water, but dissolves in hot alcohol, which eliminates hydrogen iodide, and regenerates the ethoxy-derivative.

Dipthalimidodimethyl ether, $(\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \cdot \text{CH}_2)_2\text{O}$, is prepared by

dissolving hydroxymethylphthalimide in 5—10 parts of warm phosphorus oxychloride, which is boiled during a very short period, and then rapidly cooled; it crystallises from ethylic acetate in short, snow-white prisms, and melts at 207°.

Chloromethylphthalimide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2\text{Cl}$, produced when the solution of hydroxymethylphthalimide in phosphorus oxychloride is boiled during half an hour, is insoluble in water and petroleum, dissolving with difficulty in ether, but crystallises from benzene, and melts at 132—133°.

Tribromomethylphthalimide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{N} \cdot \text{C}_2\text{H}_2\text{Br}_3$, is obtained by the direct action of bromine on ethylphthalimide and on bromethylphthalimide, and after crystallisation from chloroform melts at 190—191°. Concentrated hydrobromic acid resolves the substance into phthalic acid, ammonia, hydrogen bromide, and bromacetic acid.

M. O. F.

Synthesis of a Phosphazine. By WILHELM AUTENRIETH and OTTO HILDEBRAND (*Ber.*, 1898, 31, 1111—1113).—Phenoxythiophosphodiamide (this vol., i, 419) will not condense with benzile, but phenoxythiophosphoric dichloride, $\text{OPh} \cdot \text{PSCl}_2$ (*ibid.*), will condense with orthophenylenediamine when it (1 mol.) is first boiled with that substance (2 mols.) in ethereal solution in a reflux apparatus, the solution evaporated on the water bath, and the residue heated at 150—170° until it is quite solid and dark violet in colour. From this *P-thiophenoxyphenophosphazine*, $\text{OPh} \cdot \text{PS} \begin{smallmatrix} \diagup \text{NH} \\ \diagdown \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is obtained by extraction with ether; probably an intermediate product is formed by the reaction of one only of the two chlorine atoms. The phosphazine melts at 185°, and is a neutral, stable substance; neither aqueous alkalis nor mineral acids decompose it; prolonged boiling with alcoholic potash or strong hydrochloric acid does effect a decomposition, however.

C. F. B.

Synthesis of Aromatic Aldehydes. By LUDWIG GATTERMANN [and C. FRENZEL] (*Ber.*, 1898, 31, 1149—1152. Compare Abstr., 1897, i, 519).—Aldehydes cannot be prepared from the phenolic ethers by the method previously described, because the cuprous chloride which is necessary does not dissolve in the ethers in presence of aluminium chloride. Such aldehydes can, however, be readily obtained, and in almost theoretical amount, by the action of hydrocyanic acid and hydrogen chloride on the ether in presence of aluminium chloride. Orthotolylic methylic ether is thus first converted into the *imide*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{NH}$, the *hydrochloride* of which forms white crystals and is very unstable, decomposing when warmed with water, acids, or alkalis into ammonium chloride and the free aldehyde, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$. This compound is a colourless oil, boils at 251° and is converted by oxidation into the acid, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, melting at 192°, the constitution of which is known.

The following aldehydes have also been prepared, the yield being in

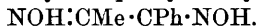
every case at least 80 per cent. of the theoretical. Methoxytolualdehyde [$\text{Me} : \text{CHO} : \text{OEt} = 1 : 3 : 6$] boils at $258-260^\circ$, whilst the *isomeride* [$\text{Me} : \text{CHO} : \text{OEt} = 1 : 2 : 5$] boils at 257° , and the third *isomeride* [$\text{Me} : \text{CHO} : \text{OEt} = 1 : 3 : 4$] boils at 250° . Methoxychlorobenzaldehyde [$\text{CHO} : \text{Cl} : \text{OMe} = 1 : 3 : 4$], from orthochloranisole, boils at 53° , and *dimethoxybenzaldehyde*, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CHO}$ [$2 : 4 : 1$], from resorcinol dimethylic ether, melts at 71° .
A. H.

Double Compounds of Aromatic Ketones with Orthophosphoric Acid. By AUGUST KLAGES and PAUL ALLENDORF (*Ber.*, 1898, 31, 1298—1301).—When an excess of a ketone is mixed with orthophosphoric acid (originally crystalline, but fused and then overcooled), or with the syrupy acid, crystals of a double compound, $\text{R} \cdot \text{CMeO} \cdot \text{H}_3\text{PO}_4$, are formed. Those compounds are stable in the presence of ether, and can even be crystallised from that solvent; they are decomposed by water or alcohol, and when distilled, or allowed to remain in the air, they lose the ketone. Benzophenone does not form such a compound, nor do those ketones in which the two ortho-positions relatively to the CMeO group are occupied by methyl groups; namely, acetylmesitylene, diacetylmesitylene, acetyldurene, diacetyldurene and acetylisodurene. Compounds were prepared with the following ketones; their melting points are quoted.

Acetophenone, $88-90^\circ$; *acetylparaxylene*, $82-83^\circ$; *acetylpsedocumene*, $132-133^\circ$; *acetylthienone*, $92-96^\circ$.
C. F. B.

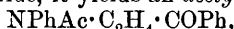
Action of Halogenated Acid Chlorides on Benzene in Presence of Aluminium Chloride. By A. COLLET (*Bull. Soc. Chim.*, 1897, [iii], 17, 66—80. Compare *Abstr.*, 1897, i, 344 and 522).—Examination of the behaviour of a number of halogenated acid chlorides, when treated with benzene in presence of aluminium chloride, shows that, however the experimental conditions may be varied, only the chlorine atom attached to the carbonyl group enters into reaction, the corresponding simple halogenated ketones being produced. In this respect they differ from the chlorinated acetic chlorides, in which the whole of the chlorine may, under certain conditions, be replaced by the phenyl group. Phenyl bromomethyl ketone, $\text{CH}_2\text{Br} \cdot \text{COPh}$, from bromoacetic chloride and benzene, is identical with the compound obtained by bromination of phenyl methyl ketone.

Phenyl α -bromomethyl ketone, $\text{CHMeBr} \cdot \text{COPh}$, from α -bromopropionic chloride, is a colourless, highly refractive oil, boiling and decomposing at $245-250^\circ$ and having a sp. gr. = 1.439 at 0° . It is insoluble in water, but miscible with most organic solvents. Potassium permanganate in alkaline solution oxidises it to benzoic acid; alcoholic ammonia converts it into diphenyldimethylparadiazine, $\text{C}_4\text{N}_2\text{Me}_2\text{Ph}_2$; and with hydroxylamine it yields phenylmethylglyoxime,

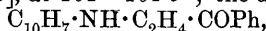


With aromatic amines in the cold or at 100° , various "anilides" are obtained, whilst at higher temperatures derivatives of indole are produced. *Phenyl anilidoethyl ketone*, $\text{NHPh} \cdot \text{C}_2\text{H}_4 \cdot \text{COPh}$, crystallises in yellow

needles melting at 98°, and forms well-defined salts. Treated with acetic anhydride or chloride, it yields an *acetyl* derivative,



melting at 55°, whilst with benzoic chloride the corresponding *benzoyl* derivative, $\text{NPhBz} \cdot \text{C}_2\text{H}_4 \cdot \text{COPh}$, melting at 103—104°, is produced. A *nitroso*-derivative, $\text{NO} \cdot \text{NPh} \cdot \text{C}_2\text{H}_4 \cdot \text{COPh}$, melting at 75°, was also prepared. *Phenyl methylanilidoethyl ketone*, $\text{NPhMe} \cdot \text{C}_2\text{H}_4 \cdot \text{COPh}$, melts at 48°; the *orthotoluidide*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{C}_2\text{H}_4 \cdot \text{COPh}$, at 89—90°; the *paratoluidide* at 90—91°; the *metaxylyl*idide, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH} \cdot \text{C}_2\text{H}_4 \cdot \text{COPh}$ [$\text{NH} : \text{Me} : \text{Me} = 4 : 1 : 3$], at 161—161.5°; the α -*naphthalide*,



at 161—163°; and the β -*naphthalide* at 120—121°. 2':3'-*Phenylmethylindole*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CMe} \\ \text{NH} \end{smallmatrix} \right\rangle \text{CPh}$, and 2'-*phenyl*-1:3'-*dimethylindole*,



are colourless, crystalline substances melting at 91—92° and 92—94° respectively. Most of the compounds just described have also been prepared from the phenyl bromethyl ketone obtained by direct bromination of phenyl ethyl ketone, which is therefore identical with the bromo-ketone produced from α -bromopropionic chloride.

The product of the action of α -bromobutyric chloride on benzene is the phenyl bromopropyl ketone, $\text{CHEtBr} \cdot \text{COPh}$, which has already been described (*loc. cit.*). It is converted by alcoholic ammonia into *diphenyldiethylparadiazine* melting at 140°, and by hydroxylamine into phenylethylglyoxime melting at 204—206°. The following new derivatives of phenyl propyl ketone have been prepared; the *metaxylyl*idide, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH} \cdot \text{CHEt} \cdot \text{COPh}$, melting at 106—107°; the α -*naphthalide*, $\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{CHEt} \cdot \text{COPh}$, melting at 137—138°; and the β -*naphthalide*, melting at 151—152°.

From α -bromisobutyric chloride and benzene, a yellowish liquid of disagreeable odour was obtained, which proved to be impure *phenyl* α -*bromisopropyl ketone*, $\text{CMe}_2\text{Br} \cdot \text{COPh}$. Phenyl isopropyl ketone, when brominated directly, yields an oily liquid of sp. gr. = 1.379 at 0° which gives benzoic acid on oxidation with alkaline permanganate, and forms an *anilido*-derivative melting at 136—137°. It is therefore either $\text{CH}_2\text{Br} \cdot \text{CHMe} \cdot \text{COPh}$ or $\text{CMe}_2\text{Br} \cdot \text{COPh}$.

Phenyl β -chloroethyl ketone, $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{COPh}$, from β -chloropropionic chloride and benzene, was not obtained sufficiently pure for analysis. It forms an *aniline* derivative melting at 111—112°.

N. L.

Brominated Ketones. By A. COLLET (*Compt. rend.*, 1897, 125, 305—306 Compare this vol., i, 139).—*Paratolyl* α -*bromomethyl ketone*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{CHBrMe}$, is obtained by gradually adding aluminium chloride (70 grams) to a mixture of α -bromopropionic chloride (50 grams) and toluene (200 grams) at the ordinary temperature; the product is poured into cold water, the toluene layer decanted and distilled, first at atmospheric pressure to remove the toluene, and later under diminished pressure, when the ketone passes over at 160—162° under

20 mm. pressure. It crystallises from boiling alcohol in small plates melting at $76-77^{\circ}$, is soluble in alcohol, benzene or toluene, and when oxidised with alkaline potassium permanganate yields terephthalic acid; it reacts with an alcoholic solution of aniline, yielding paratolyl anilidoethyl ketone, $C_6H_4Me \cdot CO \cdot CHMe \cdot NPh$, crystallising in yellow needles and melting at $104-105^{\circ}$.

Paratolyl α -bromopropyl ketone, $C_6H_4Me \cdot CO \cdot CHBrEt$, a yellow oil with a disagreeable odour, distils at $169-173^{\circ}$ under 20—25 mm. pressure, and decomposes when heated at atmospheric pressure.

Paraxylyl α -bromethyl ketone, $C_6H_3Me_2 \cdot CO \cdot CHBrMe$ [$Me_2 : CO = 1 : 4 : 2$], is an oil distilling at $166-168^{\circ}$ under 40—45 mm. pressure, and yields an *anilide* crystallising from alcohol in yellow needles and melting at 111° . The corresponding *ketone*, obtained from metaxylene, distils at $160-163^{\circ}$ under a pressure of 20—25 mm.

Diphenyl α -bromethyl ketone, $C_6H_4Ph \cdot CO \cdot CHBrMe$, forms a white, crystalline powder, melts at $79-80^{\circ}$, is soluble in hot alcohol or in acetone, and when oxidised yields diphenylparacarboxylic acid.

Benzene reacts with phenyl- $\alpha\beta$ -dibromopropionic chloride in the presence of aluminium chloride at the ordinary temperature, yielding *phenyl β -phenyl- $\alpha\beta$ -dibromomethyl ketone*, $Ph \cdot CO \cdot CHBr \cdot CHBrPh$, which crystallises in colourless needles melting at 88° . Claisen and Claparede have described a similar compound as melting at $156-157^{\circ}$ (Abstr., 1882, 511).
J. J. S.

The Cinnamic Acid Series. I. The Behaviour of Coumarin, the Coumaroles, and some other Derivatives to Metallic Sodium, and the accompanying Fluorescence Phenomena. By HERMANN KUNZ-KRAUSE (*Ber.*, 1898, 31, 1189—1193).—The author proposes to term ordinary coumarin *coumarole*, and to extend this nomenclature to its derivatives.

In the cinnamic acid series of compounds, only direct derivatives of coumarin yield sodium salts which form fluorescent aqueous solutions, the only exception being coumaric acid. Thus orthomethoxycoumaraldehyde, cinnamic acid itself, 3 : 4-dihydroxycinnamic acid, piperic acid, caffetannic acid, and piperine do not yield sodium salts of this character, whereas coumarin itself, umbelliferone, daphnetin, æsculetin, and β -methylæsculetin all form them. The author is of opinion that the fluorescence of these salts is not to be attributed to the presence of the coumarin group as such, but to the group formed from it by hydrolysis in alkaline solution, and this agrees with the fact that coumaric acid also yields a fluorescent sodium salt. β -Methylæsculetin forms two sodium compounds, $C_{10}H_8Na_2O_5$ and $C_{10}H_7Na_5O_5$, in both of which the lactone combination has been destroyed.

The solutions of derivatives of coumarin in aniline, pyridine, and quinoline are not fluorescent, and many of these compounds appear to form additive compounds with the bases named.
A. H.

New Method of Preparing 1 : 3 : 4-Xylenesulphaminic Acid. By ALFRED JUNGHAN (*Ber.*, 1898, 31, 1234—1236).—*Xylidine* 1 : 3 : 4-xylenesulphamate, $C_6H_3Me_2 \cdot NH \cdot SO_3H$, $C_6H_3Me_2 \cdot NH_2$, is ob-

tained by passing dry sulphurous anhydride into unsymmetrical metaxylidine until the gas is no longer absorbed, and heating the crystals thus obtained at $170-180^{\circ}$ during 5 hours in sealed tubes; the product is a mixture of xylidine, sulphur, and xylidine xylenesulphaminat, which crystallises from hot water in beautiful, colourless needles, and melts at $169-170^{\circ}$. The substance is also produced when chlorosulphonic acid is slowly added to a cold solution of 1:3:4-xylidine in chloroform; it is insoluble in benzene and petroleum, but dissolves readily in alcohol and in hot water, and is sparingly soluble in ether.

1:3:4-Xylenesulphaminic acid, $C_6H_3Me_2 \cdot NH \cdot SO_3H$, crystallises in pale red needles; it is obtained by treating a concentrated aqueous solution of the ammonium salt, which crystallises in white, lustrous leaflets, with half its volume of fuming hydrochloric acid. It dissolves readily in water, ethylic alcohol, and methylic alcohol, but is almost insoluble in benzene, petroleum, chloroform, and ether. The barium salt forms lustrous leaflets, and the sodium salt also crystallises in leaflets.

The acid described in this paper is the first aromatic sulphaminic acid which has been hitherto isolated. M. O. F.

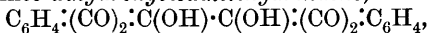
Parabenzoyltoluene Derivatives. By PAUL BOURCET (*Bull. Soc. Chim.*, 1897, [iii], 17, 81—85. Compare Abstr., 1897, i, 566).—Trinitroparabenzoyltriphenylmethane, $NO_2 \cdot C_6H_3Bz \cdot CH(C_6H_4 \cdot NO_2)_2$, is obtained by slowly adding parabenzoyltriphenylmethane to a large excess of fuming nitric acid at 0° , finally warming gently on the water bath. As precipitated from this solution by water, it is a white powder, soon becoming yellow on exposure to light, but as obtained by evaporating the nitric acid solution, it forms yellowish, monoclinic crystals. It melts at $74-75^{\circ}$, is insoluble in water and light petroleum, slightly soluble in ether and alcohol, and very soluble in benzene, chloroform, and boiling acetic acid.

Trinitroparabenzoyltriphenylcarbinol, $NO_2 \cdot C_6H_3Bz \cdot C(C_6H_4 \cdot NO_2)_2 \cdot OH$, is prepared by oxidising the preceding compound with chromic acid in acetic acid solution, and, less easily, by direct nitration of parabenzoyltriphenylcarbinol. It is a colourless substance, becoming bright red on exposure to light, and crystallises with difficulty from ether, melts at about 88° , is insoluble in water and light petroleum, fairly soluble in alcohol and ether, very soluble in chloroform, benzene, and boiling acetic acid.

Parabenzoylpararosaniline acetate, $NH_2 \cdot C_6H_3Bz \cdot C(C_6H_4 \cdot NH_2)_2 \cdot OAc$, obtained by acting on an acetic acid solution of trinitroparabenzoyltriphenylcarbinol with the theoretical quantity of zinc powder, is a green, crystalline powder, the solution of which appears red by transmitted light. It is insoluble in benzene, soluble in alcohol and acetic acid, and dyes silk, wool, and cotton a fast green without a mordant.

Parabenzoylparaleucaniline, $NH_2 \cdot C_6H_3Bz \cdot CH(C_6H_4 \cdot NH_2)_2$, is prepared by reducing trinitroparabenzoyltriphenylcarbinol with excess of zinc and acetic acid; it forms colourless crystals, insoluble in water, somewhat soluble in alcohol, which decompose without melting when heated to 115° . N. L.

Transformations of Ethinediphthalide. I. By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, 31, 1159—1174).—The formula $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH \cdot CH \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_4$, ascribed by Nathanson (*Abstr.*, 1894, i, 37) to bisdiketohydrindene, is identical with that given by Kaufmann to diphtalylethane. The authors have therefore investigated the reactions of bisdiketohydrindene and have found that they all agree with the formula of Nathanson. Bisdiketohydrindene readily yields a *potassium* salt, $C_{18}H_8K_2O_4$, which crystallises in brownish-red, quadratic plates, and is converted by methylic iodide into *dimethylbisdiketohydrindene*, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CMe \cdot CMe \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_4$, crystallising in colourless, rhombic tablets melting at 203—205°. The constitution of this compound is proved by the facts that it is not affected by boiling hydriodic acid, and that it is also formed by the oxidation of β -methylidiketohydrindene, $C_6H_4:(CO)_2:CHMe$. Bis-diketohydrindene is converted by oxidation with hydrogen peroxide in alkaline solution into *dihydroxybisdiketohydrindene*,



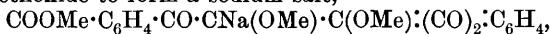
which crystallises in yellow, pointed needles melting at 168—170° and is decomposed by boiling into phthalonic acid, $COOH \cdot C_6H_4 \cdot CO \cdot COOH$,

and anhydrobisdiketohydrindene, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:C \begin{smallmatrix} \diagup CH_2 \\ \diagdown CH_2 \end{smallmatrix} CO$, the

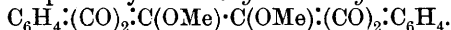
latter being probably a secondary product, formed by the action of water on the diketohydrindene primarily produced. The hydroxy-compound is converted by acetic anhydride into *bisdiketohydrindene oxide*,

$O \begin{smallmatrix} \diagup C:(CO)_2:C_6H_4 \\ \diagdown C:(CO)_2:C_6H_4 \end{smallmatrix}$, which crystallises in orange-yellow needles melting

and decomposing at 216—218°. Hydriodic acid reduces the hydroxy-compound to isoethinediphthalide. Chlorine converts bisdiketohydrindene into *dichlorobisdiketohydrindene*, $C_6H_4:(CO)_2:CCl \cdot CCl:(CO)_2:C_6H_4$, which crystallises in serrated crystals melting at about 298°. Aqueous potash converts it into the dihydroxy-compound described above, whilst hydriodic acid reduces it to bisdiketohydrindene. It reacts with sodium methoxide to form a sodium salt,

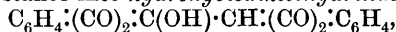


which crystallises in yellow tablets, and on acidification yields a substance which crystallises in faintly pink, rhombic tablets melting at 175—180°, and is probably *dimethoxybisdiketohydrindene*,



Dibromobisdiketohydrindene, prepared in a similar manner to the dichloro-compound, is a white powder and decomposes above 250°.

Phosphorus pentachloride converts bisdiketohydrindene into the *monochloro*-derivative, $C_6H_4:(CO)_2:CCl \cdot CH:(CO)_2:C_6H_4$, which crystallises in serrated needles melting at 242—244°. Alcoholic sodium ethoxide converts this substance into *hydroxybisdiketohydrindene*,



which crystallises in microscopic prisms melting at 171°, and is reduced by hydriodic acid to isoethinediphthalide and a second compound, $C_{18}H_{12}O_4$, which crystallises in colourless needles melting at 150°.

Sodium methoxide converts the monhydroxy-compound into a *sodium* salt, $\text{OMe} \cdot \text{C}_{18}\text{H}_8\text{NaO}_4 + \frac{1}{2}\text{H}_2\text{O}$, which on acidification yields *methoxybisdiketohydrindene*, $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{CH} \cdot \text{C}(\text{OMe}) : (\text{CO})_2 : \text{C}_6\text{H}_4$; this crystallises in flat prisms and melts and decomposes at about 230° . The crystalline *silver* salt is converted by methylic iodide into *methoxymethylbisdiketohydrindene*, $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{CMe} \cdot \text{C}(\text{OMe}) : (\text{CO})_2 : \text{C}_6\text{H}_4$, crystallising in colourless tablets melting at $214\text{--}216^\circ$. A. H.

Transformations of Ethinedipthalide. II. By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, 31, 1272—1286).—*Isoethinedipthalide* (preceding abstract) is shown to be probably *di-*

hydroxynaphthalacenequinone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, this formula being most in harmony with the reactions described below. It has been compared carefully with Kaufmann's indenigo (*Abstr.*, 1897, i, 245), and the two substances appear to be identical, in which case the latter can no longer be regarded as diphtalylethylene.

Isoethinedipthalide is oxidised to phthalic acid by hydrogen peroxide in boiling alkaline solution. With potash, it forms a *potassium* salt, $\text{C}_{18}\text{H}_9\text{KO}_4$, dark bronze coloured and shot with green, but this is not acted on by potash, even at 300° ; when heated with soda-lime at $390\text{--}400^\circ$ in a bath of saltpetre, isoethinedipthalide is, however, partly resolved into phthalic and benzoic acids. Hydrochloric acid at 250° has no action on it.

When isoethinedipthalide is oxidised with fuming nitric acid at 100° , phthalic acid is formed. At the ordinary temperature, it yields a brown substance melting at $330\text{--}333^\circ$, which appears to be *naphthacenediquinone*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{CO} \cdot \text{C} \cdot \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$; it is reconverted into isoethinedipthalide by reduction with hydriodic acid and phosphorus, or by heating with potash at 300° , or boiling with 33 per cent. aqueous potash.

When distilled with zinc dust, isoethinedipthalide is reduced to *naphthalene*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \cdot \text{C} \cdot \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{C} \cdot \text{CH} \end{smallmatrix} \text{C}_6\text{H}_4$, and *dihydronaphthalene*,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \cdot \text{C} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH} \cdot \text{C} \cdot \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_4$; the latter of these is more soluble in benzene, and it is the product formed when isoethinedipthalide is reduced with hydriodic acid and phosphorus at $154\text{--}157^\circ$. Dihydronaphthalene melts at $206\text{--}207^\circ$ and boils at about 400° ; it is oxidised by chromic acid in boiling acetic acid solution to *naphthalacenequinone*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{CH} \cdot \text{C} \cdot \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, which is yellow, melts at 294° , and is converted by potash at 310° , into benzoic and 2-naphthoic acids and some isoethinedipthalide; by fuming nitric acid in acetic acid solution, into a yellow *mononitronaphthalacenequinone* melting at 315° , and by distillation with zinc dust into naphthalene and dihydronaphthalene; with fuming nitric acid in acetic acid solution, dihydronaphthalene yields a *mononitronaphthalacenequinone* melting at about 240° . Naphthalene

forms orange-yellow to reddish-yellow leafy crystals and melts near 335° , the exact temperature depending on the rate of heating; with fuming nitric acid in acetic acid solution it appears to yield naphthacenequinone; distilled with zinc dust it yields dihydronaphthacene.

Isoethinidiphthalide forms orange-yellow *diacetyl* and *dibenzoyl* derivatives; these melt and decompose at 220 — 235° and 334 — 339° respectively. With a mixture of phosphorus oxychloride and pentachloride at 145° , it yields yellowish *dichloronaphthacenequinone*, $C_6H_4 \begin{smallmatrix} \diagup CCl \cdot C \cdot CO \\ \diagdown CCl \cdot C \cdot CO \end{smallmatrix} C_6H_4$; this melts at 259 — 260° (corr.), yields with aniline the brown *dianilidonaphthacenequinone* melting at 245° , and is reduced by hydriodic acid and phosphorus to dihydronaphthacene.

C. F. B.

Allofluorescein. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, 31, 1302).—A reply to R. Meyer (this vol., ii, 275).

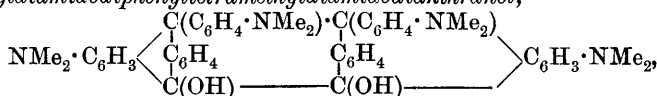
The description of allofluorescein as a colourless, amorphous substance (*Abstr.*, 1896, i, 50) is erroneous; under the microscope it is seen to be crystalline.

C. F. B.

Ethenyltriamidonaphthalene and its Acetyl Compound. By OSCAR MARKFELDT (*Ber.*, 1898, 31, 1174—1178).—The primary azo-colouring matters derived from ethenyltriamidonaphthalene are only of small value, but the secondary disazo-compounds are not less valuable than the benzidine colouring matters, and dye unmordanted cotton, even in acid solution. Meldola and Streatfeild were unable to prepare an acetyl derivative of the base (*Trans.*, 1887, 691), but this can readily be obtained by heating it with acetic anhydride and fused sodium acetate. The *acetate*, $CMe \begin{smallmatrix} \diagup NH \\ \diagdown N \end{smallmatrix} C_{10}H_5 \cdot NHAc, C_2H_4O_2$, crystallises with 2 mols. of acetic acid in white, nacreous plates melting above 280° , whilst the *acetyl base* crystallises with $2H_2O$ in snow-white needles, with a satin lustre. The water is lost at 110° , and the anhydrous base then melts above 280° . *Acetylenyltriamidonaphthalene hydrochloride* dissolves without decomposition in water, and crystallises in flat, white needles which become pink in the air. The *sulphate*, *nitrate*, and *picrate* have all been obtained well crystallised.

A. H.

Symmetrical Tetramethyldiamidodiphenyltetramethyldiamidodanthranol and the corresponding Oxanthranol. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1897, 125, 286—288. Compare O. Fischer, *Abstr.*, 1881, 587).—The condensation attempted by Fischer from tetramethyldiamidodiphenylmethaneorthocarboxylic acid is readily accomplished by using dimethylaniline and phosphorus oxychloride in place of sulphuric acid. The product, *symmetrical tetramethyldiamidodiphenyltetramethyldiamidodanthranol*,



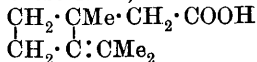
crystallises from boiling toluene in yellow plates containing a molecule of toluene of crystallisation, which it loses when dried at 130° ; it

melts at 275° and is readily oxidised, so much so that, on heating, it becomes phosphorescent. When an acid solution of this compound is oxidised with potassium dichromate, or with ferric chloride, an intense pure blue coloration is obtained; this is very fugitive, the colour slowly disappearing in the cold, and rapidly on heating. From concentrated solutions, colourless needles of *tetramethyldiamidophenyl-oxanthranol* are deposited; these dissolve readily in chloroform or nitrobenzene, but are only sparingly soluble in alcohol, ether, benzene, or toluene; they melt at 213° and dissolve in concentrated sulphuric acid, yielding a blue solution. The fugitive blue colour first formed is the chloride of the colourless carbinol, and its acid solution, on warming, is hydrolysed into the colourless oxanthranol and hydrochloric acid. The compound of the blue colouring matter with zinc chloride is more stable, and crystallises in small, bronzy needles, which, however, slowly turn colourless.

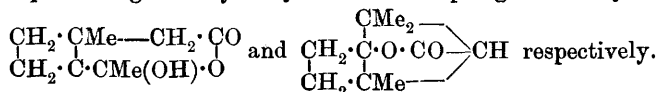
J. J. S.

Terpenes and Ethereal Oils. Pulegenic Acid and Synthetical Pulegone. By OTTO WALLACH (*Annalen*, 1898, 300, 259—277. Compare Abstr., 1896, i, 310).—*Methylic pulegenate* boils at 89 — 90° under a pressure of 10 mm.; it is prepared by the action of sodium methoxide dissolved in methylic alcohol on the hydrochloride. On acidifying the alkaline liquid which remains after methylic alcohol and the ethereal salt have been removed in a current of steam, the *lactone*, $C_{10}H_{16}O_2$, is precipitated; it boils at 125 — 127° under a pressure of 15 mm. The *acid*, $C_{10}H_{16}O_2$, produced along with it, boils at 145 — 147° and 256 — 260° under pressures of 15 mm. and 760 mm. respectively; it has the sp. gr. = 0.9955, and the refractive index $n_D = 1.47547$ at 21° . Although closely resembling pulegenic acid, the substances are not identical, as the *amide* crystallises from very dilute methylic alcohol in needles, and melts at 152° .

Pulegenolide, $C_{10}H_{14}O_2$, produced by the action of alcoholic sodium methoxide on the brominated lactone obtained from pulegenic acid and potassium hypobromite, melts at 44 — 45° , and boils at 265 — 268° under atmospheric pressure. The *hydroxy-acid*, $C_{10}H_{16}O_3$, produced on hydrolysing the lactone with aqueous alkali, melts at 95° , and forms a *silver* salt. The hydroxylactone, $C_{10}H_{16}O_3$, obtained by oxidising pulegenic acid with potassium permanganate (*loc. cit.*), may be converted into pulegenolide by the action of phosphorus pentachloride and subsequent treatment of the product with alcoholic sodium methoxide; conversely, the brominated lactone obtained from pulegenic acid and potassium hypobromite yields the hydroxy-lactone under the influence of moist silver oxide. In view of these facts, the author ascribes to pulegenic acid the constitution



representing the hydroxy-lactone and pulegenolide by the formulæ



The remaining portion of the paper deals with compounds described in a preliminary communication (Abstr., 1897, i, 159). M. O. F.

Terpenes and Ethereal Oils. *Cis- and trans-Isomerism in the Menthol Series.* By OTTO WALLACH [and D. F. WERNER] (*Annalen*, 1898, 300, 278—285. Compare Abstr., 1893, i, 724).—In view of the fact that dextrorotatory menthylamine yields a large proportion of menthene under the influence of nitrous acid, whilst *l*-menthol arises from the *levo*-base, it follows that the menthol corresponding to dextrorotatory menthylamine loses water more readily than that derived from *levo*-menthylamine. The latter is therefore referred to as *trans*-menthylamine, the dextrorotatory base being called *cis*-menthylamine.

trans-Menthylamine boils at 209—210°; it has sp. gr. = 0·86, and the refractive index $n_D = 1·46058$ at 20°. The *carbamide* melts at 134—136°, and the *phenylcarbamide*, crystallises from alcohol, and melts at 140—141°.

trans-Menthylmethylnitrosamine, $C_{10}H_{19} \cdot NMe \cdot NO$, is a yellow oil which boils at 145—146° under a pressure of 18—20 mm. *trans*-Menthylethylnitrosamine, $C_{10}H_{19} \cdot NEt \cdot NO$, crystallises from dilute methylic alcohol in colourless needles, melts at 52—53°, and boils at 155—156° under a pressure of 22 mm. *trans*-Menthylpropylnitrosamine, $C_{10}H_{19} \cdot NPr^a \cdot NO$, boils at 159—161° under a pressure of 20 mm. *trans*-Menthylisobutylnitrosamine, $C_{10}H_{19} \cdot N(C_2H_5) \cdot NO$, forms white needles, melts at 52—53°, and boils at 160—161°.

trans-Menthyltrimethylammonium iodide, $C_{10}H_{19} \cdot NMe_3I$, separates from water in large, colourless crystals, and melts at 190°; the *triiodide* melts at 117—118°. *trans*-Menthyltrimethylammonium hydroxide, $C_{10}H_{19} \cdot NMe_3 \cdot OH$, is a colourless, crystalline, hygroscopic mass; distillation under atmospheric pressure resolves it into water, trimethylamine, and menthene.

cis-Menthylamine was previously obtained (*loc. cit.*) by heating *l*-menthone with ammonium formate, when a mixture of the *levo*- and dextro-rotatory formylmenthylamines was produced, these being separated by fractional crystallisation. In attempting to utilise the acetyl derivative for this purpose, it was found that the compound must be heated with hydrochloric acid in a sealed tube at 140° before being completely hydrolysed.

cis-Menthylamine boils at 207—208°, has sp. gr. = 0·857, and the refractive index $n_D = 1·45940$. The *carbamide* and the *phenylcarbamide* melt at 155—156° and 177—178° respectively. *cis*-Menthyltrimethylammonium iodide crystallises from water, and melts at 160—161°; *cis*-menthyltrimethylammonium hydroxide is resolved into water, trimethylamine, and menthene on distillation. Menthene is also formed when an aqueous solution of *cis*-menthylamine hydrochloride is boiled with sodium nitrite.

M. O. F.

Terpenes and Ethereal Oils. Pinocamphone, a New Camphor from Pinene. By OTTO WALLACH [and J. A. SMYTHE] (*Annalen*, 1898, 300, 286—293).—Pinocarvone is the name now given to the ketone, $C_{10}H_{14}O$, obtained by oxidising pinocarveol, $C_{10}H_{15} \cdot OH$, derived from pinyamine (Wallach, Abstr., 1894, i, 45); the *semicarbazone* of pinocarvone crystallises from dilute methylic alcohol, and melts at 204°.

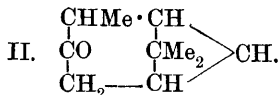
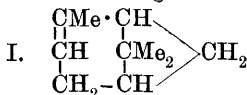
Pinocamphone, $C_{10}H_{16}O$, is a bye-product in the preparation of pinylamine from nitrosopinene, zinc dust, and glacial acetic acid, and represents 20 per cent. of the material employed; it has the odour of turpentine, and suggests peppermint oil when heated. The ketone boils at $211-213^\circ$ under atmospheric pressure; it has the sp. gr. = 0.959, and the refractive index $n_D = 1.47273$ at 21° . The *semicarbazone* melts at $199-200^\circ$, and the *oxime* is volatile in an atmosphere of steam, crystallises in large, transparent plates, and melts at $86-87^\circ$.

Pinocampeol, $C_{10}H_{17} \cdot OH$, is obtained by reducing pinocamphone with sodium in aqueous ether, and forms a viscous liquid having the odour of terpineol and turpentine; it boils at $218-219^\circ$, has the sp. gr. = 0.9655, and the refractive index $n_D = 1.48612$ at 20° . The *phenylurethane* melts at 98° .

Pinocamphonitrile, $C_{10}H_{15}N$, is the product of treating pinocamphone-oxime with boiling sulphuric acid (1:1); a portion of the oxime remains unchanged.

Reduction of nitrosopinene bromide has yielded a *ketone*, $C_{10}H_{16}O$, isomeric with pinocamphone, and having the odour of carvone; it closely resembles the inactive dihydrocarvone, and the *oxime* melts at $113-114^\circ$. A *base* is formed along with it which boils at $217-220^\circ$, and has the sp. gr. = 0.918.

Representing pinene by the formula I, the author regards pinocamphone as having the constitution II.



M. O. F.

Terpenes and Ethereal Oils. Fenchone. By OTTO WALLACH (*Annalen*, 1898, 300, 294—322. Compare Abstr., 1895, i, 380).—The difficulties hitherto attending the production of purified fenchocarboxylic acid have now been removed. There are found to be two isomeric acids of this description, distinguished by the author as α - and β -fenchocarboxylic acids. In order to separate these two substances, the crude product of the action of carbonic anhydride on an ethereal solution of fenchone in presence of sodium is submitted to distillation under a pressure of 15 mm., the fraction which boils at $150-180^\circ$ solidifies in the receiver, and consists of the isomeric fenchocarboxylic acids along with small quantities of hydroxycarbonylfenchone (see below), and the anhydro-acid, $C_{11}H_{16}O_2$. The mixture is therefore treated with ammonia or caustic soda, agitated with ether, and the aqueous liquor acidified; α -fenchocarboxylic acid crystallises from the product more rapidly than the β -derivative, which is also more readily soluble in light petroleum than the isomeride; this is therefore washed with this agent, and finally crystallised from dilute acetic acid.

α -Fenchocarboxylic acid, $OH \cdot C_{10}H_{16} \cdot COOH$, crystallises from acetic acid in transparent prisms, and melts at $141-142^\circ$, although this

constant is very materially depressed by contamination with the β -acid; it boils at 175° under a pressure of 11 mm., and does not undergo decomposition. The *lead* salt is readily soluble in ether, which also dissolves the *silver* salt; the latter is almost insoluble in water, but dissolves in chloroform and in methylic iodide. α -Fenchocarboxylic acid is optically active, a 4.5 per cent. ethereal solution having the specific rotatory power $[\alpha]_D = +11.28^\circ$. On mixing equal weights of the acid obtained from *d*-fenchone and from *l*-fenchone, an inactive *racemic acid* is produced, which melts at 91 – 92° .

Anhydrofenchocarboxylic acid, $C_{11}H_{16}O_2$, is formed on distilling α -fenchocarboxylic acid under atmospheric pressure, water being eliminated; it dissolves with great difficulty in water, and is volatile in an atmosphere of steam, differing in this respect from α -fenchocarboxylic acid. The substance boils at 275 – 277° under atmospheric pressure, and, after crystallisation from dilute acetone, melts at 175° ; the *lead* salt is insoluble in ether. The anhydro-acid is also formed when α -fenchocarboxylic acid is fused with potash.

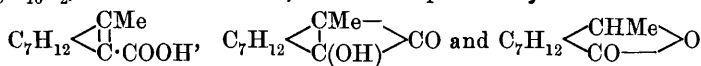
Hydroxycarbofenchonone, $C_{11}H_{16}O_2$, the yellow ketone obtained on distilling *lead* α -fenchocarboxylate in a vacuum, crystallises from petroleum in yellow, transparent plates or prisms, having the appearance of a uranium salt, has a feeble, camphor-like odour, melts at 96° , and boils at 273 – 274° under atmospheric pressure. The *oxime* crystallises from methylic alcohol in colourless, transparent needles, and melts at 108° ; reduction with sodium in alcoholic solution converts it into a *base* which melts at 74° , and is not volatile in an atmosphere of steam. The *compound*, $C_{11}H_{17}NO$, is obtained by the action of ammonia on the ketone, which loses its yellow colour; the substance separates from alcohol in colourless crystals, and melts at 205° . The yellow ketone dissolves in warm caustic soda, undergoing conversion into β -fenchocarboxylic acid; it is probably a cyclic orthohydroxyketone.

β -Fenchocarboxylic acid is prepared by digesting hydroxycarbofenchonone with excess of warm, dilute caustic soda on the water bath until dissolution is complete, and the liquid is almost colourless; it separates in opaque, indefinite crystals on diluting the acetic acid solution, and melts at 76 – 77° . The acid is dextrorotatory, but is less active than the isomeride; it is also less stable, yields fenchylic alcohol and anhydrofenchocarboxylic acid when heated under atmospheric pressure, and is in part converted into the α -acid in a vacuum. Sodium hypobromite or an acid solution of potassium permanganate give rise to fenchone. The *lead* and *silver* salts do not differ very materially from those of the isomeric acid. The α - and β -fenchocarboxylic acids may be regarded as the *trans*- and *cis*-modifications respectively.

The *lactone*, $C_{10}H_{16}O_2$, is obtained by oxidising α -fenchocarboxylic acid with an amount of potassium permanganate corresponding with three atomic proportions of oxygen; it crystallises from dilute methylic alcohol, and melts at 64.5° , boiling at 150° under a pressure of 14 mm.

Representing fenchone by the formula $C_7H_{12} \begin{array}{c} \diagup CHMe \\ | \\ CO \end{array}$, the fenchone-

carboxylic acids have the constitution $C_7H_{14} \begin{smallmatrix} \text{CHMe} \\ | \\ \text{C}(\text{OH}) \cdot \text{COOH} \end{smallmatrix}$; anhydrofenchocarboxylic acid, hydroxycarbofenchonone, and the lactone, $C_{10}H_{16}O_2$, which are isomeric, are then expressed by the formulæ



respectively.

Methylic fencholenate *hydrochloride*, $C_9H_{16}Cl \cdot COOMe$, is obtained by saturating a solution of fencholenic acid in methylic alcohol with hydrogen chloride; it boils at $124-125^\circ$ under a pressure of 14 mm. *Methylic* fencholenate, $C_9H_{15} \cdot COOMe$, is produced when the hydrochloride is treated with sodium methoxide; it boils at $97-98^\circ$ under a pressure of 13 mm., and has an agreeable, geranium-like odour.

Fencholenic alcohol, obtained by reducing the amide with sodium in ethylic alcohol (Abstr., 1895, i, 381), is not identical with the compound obtained by the action of nitrous acid on fencholenamine (Abstr., 1892, 1240). The latter boils at $94-96^\circ$ under a pressure of 20 mm., has sp. gr. = 0.922, and the refractive index $n_D = 1.4732$; it does not yield fenchene when treated with hot dilute sulphuric acid.

Fenchelene, $C_{10}H_{16}$, is a bye-product in the formation of fencholenic alcohol, and boils at $66-70^\circ$ and $175-178^\circ$ under pressures of 20 mm. and 760 mm. respectively; it has sp. gr. = 0.842, and the refractive index $n_D = 1.47439$ at 20° .

The *lactone*, $C_{10}H_{16}BrO_2$, is obtained by the action of potassium hypobromite on a solution of potassium fencholenate; it crystallises from light petroleum, and melts at 56° .

Hydroxyfenchenic acid, $OH \cdot C_9H_{14} \cdot COOH$, is the chief product of oxidising fenchene with potassium permanganate; it melts at $152-153^\circ$ (compare Abstr., 1891, 1086).

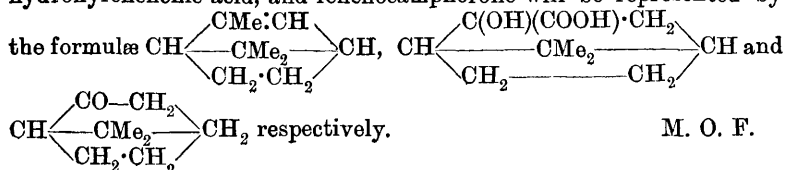
Fenchocamphorone, $C_9H_{14}O$, is obtained by the oxidation of hydroxyfenchenic acid with sodium hypochlorite, chromic acid, potassium permanganate, or lead peroxide with sulphuric acid; it melts at $109-110^\circ$, and boils at 202° . The ketone is isomeric with phorone, and has the odour of camphor, from which it is distinguishable with difficulty. The *oxime* melts at $69-71^\circ$, and yields a nitrile on treatment with dilute sulphuric acid.

Fenchocamphorol, $C_9H_{15} \cdot OH$, results on reducing fenchocamphorone with sodium in aqueous ether; it crystallises from dilute methylic alcohol in needles, and melts at $128-130^\circ$.

Fenchocamphorone is oxidised by dilute nitric acid (sp. gr. = 1.25), yielding two acids which crystallise from water, and melt at 124° and 202° respectively; the latter compound probably has the composition $C_9H_{14}O_4$, and yields a silver salt which shows it to be dibasic.

The author considers that the formula $CH \begin{smallmatrix} \text{CHMe} \cdot \text{CO} \\ | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} CH$ represents the structure of fenchone more accurately than the expression

already suggested (Abstr., 1895, i, 382). If this is accepted, fenchene, hydroxyfenchenic acid, and fenchocamphorone will be represented by



M. O. F.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1898, 300, 322—357. Compare this volume, i, 89).—Usnic acid is found in *Cladina silvatica* (L.), *Cl. alpestris* (Rabenh.), and in *Cladonia amaurocraea* (Flörke); contrary to the statement of Rochleder and Heldt, genuine *Cladonia rangiferina* (L.) contains no trace of this acid.

Gyrophoric acid, hitherto only recognised by Stenhouse in *Umbilicaria pustulata* (L.) and *Ochrolechia tartarea* (L.), has now been found in *Gyrophora hirsuta* (Ach.) and *G. deusta* (L.).

Umbilicatic acid occurs in *Gyrophora polyphylla* (L.), *G. hyperborea* (Hoffm.), and in *G. deusta* (L.).

Cetraria fahlunensis (Ach.), *Cladina rangiferina* (L.), and *Cl. silvatica* (L.) contain cetraric acid, previously found in *Cetraria islandica* (L.).

The author has already enumerated forty-one lichens which contain atranoric acid; to these must be added *Sphyridium placophyllum* (Nahlbg.), *Cladina rangiferina* (L.), *Parmelia acetabulum* (Neck.), and *Cetraria fahlunensis* (Ach.).

Salazinic acid has been found in *Stereocaulon salazinum* (Bory), *Alectoria cana* (Ach.), *Parmelia perforata* (Ach.), *P. excrecens* (Arnold), *P. conspersa* (Ehrh.), and *Everniopsis Trulla* (Ach.); it has been also recognised in *Parmelia acetabulum*.

Hæmatomma ventosum (L.) contains divaricatic acid. *Divaricatinic acid* is produced along with orcinol, when this substance is heated with dilute caustic potash; it crystallises from benzene in microscopic, lustrous prisms, and melts at 149°, evolving gas.

Hesse's coccellic acid, occurring in *Cladonia coccifera*, has been found by the author in *Cl. amaurocraea* (Flörke).

Sphærophorin, which melts at 138—139°, and *sphærophoric acid* have been isolated from *Sphærophorus fragilis* (L.) and *Sph. coralloides* (Pers.); the first-named lichen contains also *fragilin*, a golden-yellow substance resembling lichen-chrysophanic acid and other derivatives of anthracene in its colour reactions.

Physodalic acid and *physodalin* have been obtained from *Parmelia physodes* and *Parmelia pertusa* (Schrk.).

Mannitol has been found in *Calloposma vitellinum* (Ehrh.).

M. O. F.

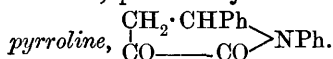
Action of Benzylideneaniline on the Ethereal Salts of Unsaturated α -Hydroxy-acids. By ROBERT SCHIFF and L. GIGLI (*Ber.*, 1898, 31, 1306—1310).—In a preceding abstract (this vol., i, 464), reasons are given for supposing that the ethereal salts of so-called α -ketonic acids

really exist in the α -hydroxy (enolic) form, $\text{CHR}:\text{C}(\text{OH})\cdot\text{COOEt}$. These salts are known, in the case of ethylic oxaloacetate, $[\text{R} = \text{COOEt}]$, to form compounds with benzylideneaniline, $\text{CHPh}:\text{NR}'$ [$\text{R}' = \text{Ph}$], (Abstr., 1897, i, 293); such compounds must be regarded as α -hydroxy-

pyrrolones, $\begin{array}{c} \text{CR}\cdot\text{CHPh} \\ | \\ \text{C}(\text{OH})\cdot\text{CO} \end{array} \gg \text{NR}'$, in this particular case, as the enolic form of ethylic diphenyldihydrodiketopyrrolinecarboxylate. Similar enolic forms, enumerated below with their decomposing points, have been prepared by fusing benzylideneaniline (or β -naphthylamine) with various ethylic salts; all of them, in benzene solution, give a blood-red coloration with ferric chloride; when warmed with excess of free hydroxylamine, they are converted, according to the authors, into the ketonic forms, which then yield monoximes.

3-Acetyl-1:2-diphenyldiketodihydropyrroline, $[\text{R} = \text{Ac}; \text{R}' = \text{Ph}]$, 239—240°; oxime, 213—215°. 3-Benzoyl-1:3-diphenyldiketodihydropyrroline, $[\text{R} = \text{Bz}; \text{R}' = \text{Ph}]$, 250—252°; oxime, 213—215°. 3-Benzoyl-2-phenyl-1- β -naphthyl diketodihydropyrroline, $[\text{R} = \text{Bz}; \text{R}' = \text{C}_{10}\text{H}_{17}(\beta)]$, 252—254°. 3-Cinnamoyl-1:2-diphenyldiketodihydropyrroline, $[\text{R} = \text{CO}\cdot\text{CH}:\text{CHPh}; \text{R}' = \text{Ph}]$, 230—231°; this substance was prepared from ethylic benzylideneacetoneoxalate, $\text{CHPh}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{COOEt}$, which was itself obtained by condensing benzylideneacetone with ethylic oxalate, in cooled alcoholic solution, by means of sodium ethoxide, is yellow, melts at 84°, gives a coloration with ferric chloride, and condenses with phenylhydrazine, when warmed with it in acetic acid solution, to a compound, $\text{CHPh}:\text{CH}\cdot\text{C} \begin{array}{c} \text{N}-\text{NPh} \\ \diagup \quad \diagdown \\ \text{CH}:\text{C}\cdot\text{COOEt} \end{array}$, melting at 120°.

With pyruvic acid, a substance which exists in the ketonic form and gives no coloration with ferric chloride, benzylideneaniline does not condense readily; the product is an unstable, half-solid substance, decomposing at 147—148°, and giving no coloration with ferric chloride; presumably it is the ketonic form of diphenyldiketodihydropyrroline,

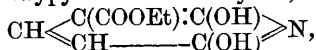


C. F. B.

Pyridine Derivatives of Ethylic Cyanacetate. By GIORGIO ERRERA (*Ber.*, 1898, 31, 1241—1246. Compare this vol., i, 297).—Ethylic 2:6-dihydroxydinicotinate, $[\text{2:6-dihydroxypyridine-3:4-dicarboxylate}]$, $\text{CH} \begin{array}{c} \text{C}(\text{COOEt})\cdot\text{C}(\text{OH}) \\ | \\ \text{C}(\text{COOEt})\cdot\text{C}(\text{OH}) \end{array} \gg \text{N}$, produced when the diamide of ethylic dicarboxyglutaconate (this vol., i, 289) is dissolved in concentrated sulphuric acid, crystallises from water, alcohol, and benzene, and melts at 199° (compare Guthzeit, Abstr., 1894, i, 71). The salt is also formed by the action of caustic soda on ethylic cyanocarboxyglutaconate, $\text{C}(\text{COOEt})_2\cdot\text{CH}\cdot\text{CNa}(\text{CN})\cdot\text{COOEt}$, the condensation product of ethylic ethoxymethylenemalonate with ethylic cyanacetate; the sodium derivative contains $2\text{H}_2\text{O}$, which is lost at 130°. When the salt or the diamide of ethylic dicarboxyglutaconate is boiled with dilute caustic soda (2 mols.), the sodium salt of monethylic 2:6-di-

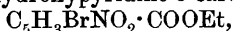
hydroxydinicotinate, $\text{CH} \begin{smallmatrix} \diagup \text{C}(\text{COOH}) : \text{C}(\text{OH}) \\ \diagdown \text{C}(\text{COOEt}) \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{N}$, is produced; it dissolves readily in hot alcohol and water, crystallising in colourless, microscopic needles containing $2\text{H}_2\text{O}$.

Ethylic 2 : 6-dihydroxypyridine-3-carboxylate,



is obtained by eliminating carbonic anhydride from the foregoing substance, and crystallises from alcohol in colourless needles melting at 179° , when it becomes red and evolves gas; the *sodium* salt is crystalline.

Ethylic bromo-2 : 6-dihydroxypyridine-3-carboxylate,

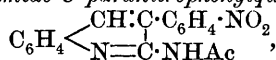


is prepared by the action of bromine water on an aqueous solution of ethylic dihydroxypyridinecarboxylate; it crystallises from alcohol in white needles, and becomes black at 200° .

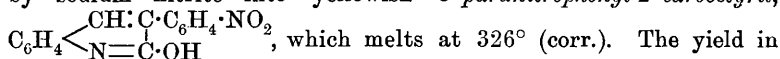
2 : 6-Dihydroxypyridine, $\text{CH} \begin{smallmatrix} \diagup \text{CH} : \text{C}(\text{OH}) \\ \diagdown \text{CH} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{N}$, obtained from ethylic dihydroxypyridinecarboxylate and excess (3 mols.) of caustic soda, crystallises from water, and melts at 195° . It is identical with the compound obtained by Ruhemann, on boiling ethylic dihydroxydinicotinate with concentrated hydrochloric acid. The *hydrochloride* forms colourless, transparent needles, and melts, evolving gas, at 193° .

M. O. F.

New Synthesis of 2'-Amidoquinoline. By ROBERT PSCHORR (*Ber.*, 1898, 31, 1289—1298).—*α-Paranitrophenylorthacetamidocinnamitrile*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, obtained by adding 10 per cent. alcoholic sodium ethoxide to a solution of orthacetamidobenzaldehyde and paranitrobenzyl cyanide in alcohol at $50\text{--}45^\circ$, is yellow, and melts at $214\text{--}215^\circ$ (corr.). When it is mixed, in alcoholic solution, at the ordinary temperature, with some caustic soda, it is converted into *2'-acetamido-3'-paranitrophenylquinoline*,



which melts at $219\text{--}220^\circ$ (corr.). If the reaction is carried out at 100° , the product is *2'-amido-3'-paranitrophenylquinoline*, which can also be obtained from the acetamido-compound by the action of hydrochloric acid at 100° ; this is yellow and melts at 258° (corr.); its picrate decomposes at about 270° ; in acetic acid solution, it is converted by sodium nitrite into yellowish *3'-paranitrophenyl-2'-carbostyryl*,



these reactions is about 60 per cent. of the theoretical. *2'-Amido-3'-phenylquinoline* and *2'-amidoquinoline* itself can be prepared in the same way; the transformation is best effected by sodium ethoxide in alcoholic solution and with the aid of heat; under these circumstances, the acetyl group is eliminated at the same time, and no acetamidoquinoline is obtained.

2'-Amido-3'-phenylquinoline is obtained by boiling an alcoholic solu-

tion of 2-acetamidobenzaldehyde and bepzylic cyanide with sodium ethoxide for a short time, and diluting the cooled product with water; it melts at 155—156° (corr.), and boils above 360°, almost without decomposing; its *picrate* melts at 234°. It yields 3'-phenyl-2'-carbostyryl, identical with the substance obtained from 2-amidobenzaldehyde and sodium phenylacetate at 130°; this melts at 235° (corr.).

Orthamidocinnamonitrile is yellowish and melts at 134—135° (corr.); its *picrate* melts at 192—193° (corr.), its *acetyl* derivative at 172—174° (corr.). 2'-Amidoquinoline melts at 129° (not 114°, Ephraim, Abstr., 1891, 1510); the *picrate* decomposes at 250—253° (corr.). The nitrile could not be obtained from 2-amidobenzaldehyde and acetonitrile; it was prepared from orthonitrocinnamic acid by treating this with phosphorus oxychloride and pentachloride, converting the chloride, in benzene solution by a current of gaseous ammonia, into the *orthonitrocinnamic amide*, which melts at 185° (corr.); and boiling this with thionyl chloride in toluene solution, or, better, distilling it with phosphoric anhydride, when *orthonitrocinnamonitrile*, melting at 92° (corr.) and boiling at 194—196° under 7—8 mm. pressure, is obtained, and can be reduced to the amido-compound in alcoholic solution by tin and hydrochloric acid.

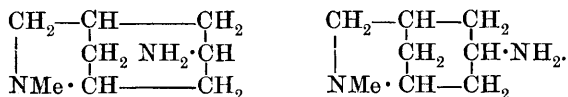
C. F. B.

Ketones of the Tropine Group. IX. The Tropolamines. By RICHARD WILLSTÄTTER and WILHELM MÜLLER (*Ber.*, 1898, 31, 1202—1214. Compare this vol., i, 159).—Tropinonoxime can be converted by different methods of reduction into two different isomeric tropylamines. *ψ-Tropylamine*, $C_8NH_{14} \cdot NH_2$, is produced when the oxime is reduced by metallic sodium and boiling amylic alcohol, and is an oil which boils at 213° (corr.), and has a slight smell of piperidine; it readily unites with atmospheric carbonic anhydride, forms a cloud with hydrogen chloride, and is miscible with ether, alcohol, and water. It is a strong diacid base and precipitates hydroxides from the solutions of many metallic salts. The *hydrochloride*, *hydrobromide*, and *hydriodide* are readily soluble in water; the *auerochloride* melts and decomposes at 223—224°, and the *platinochloride* crystallises with $2H_2O$ in rhombohedral plates, which become anhydrous at 105°, and melt and decompose at 257°. The *carbamate* can be sublimed in long needles, whilst the *dithiocarbamate*, $C_8NH_{15} \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} CS$, crystallises in lustrous plates which melt and decompose at 204—205°. *ψ-Tropyl-phenylthiocarbamide*, $C_8NH_{14} \cdot NH \cdot CS \cdot NHPh$, crystallises in lustrous prisms melting at 172°. *ψ-Tropylamine* is unaltered by prolonged boiling with a concentrated solution of sodium amyloxide.

Tropylamine is produced when tropinonoxime is reduced by sodium amalgam in acetic acid solution, and closely resembles the *ψ*-compound. It is an oil which boils at 211° (corr.) and forms readily soluble salts with the halogen acids. The *picrate* crystallises in characteristic plates which melt and decompose at 235°. The *platinochloride* is much less soluble than that of the *ψ*-base, and yields anhydrous crystals melting and decomposing at 257°. The *dithiocarbamate* crystallises in characteristic aggregates of small plates and melts at 194—195°.

Tropylphenylthiocarbamide crystallises in tablets, prisms, and needles, and melts at 142—143°. When tropylamine is boiled with a concentrated solution of sodium amyloxide in amylic alcohol, it is to a great extent converted into ψ -tropylamine, a small residue of the original base being, however, always left.

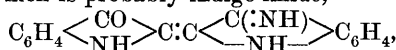
The authors propose the following formulæ for these two compounds, which they regard as geometrically isomeric.



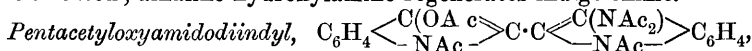
A. H.

Indigo-oxime. By JOHANNES THIELE and ROBERT H. PICKARD (*Ber.*, 1898, 31, 1252—1253).—Finely divided indigo is warmed with caustic soda on the water bath, and in a vessel from which the air has been driven out by hydrogen, and agitated with 2 parts of hydroxylamine hydrochloride; on filtering the liquid into cold, dilute hydrochloric acid, *indigo-oxime*, $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_2$, separates as a brownish-violet, voluminous precipitate; it is washed with boiling water, and recrystallised from alcohol, separating in small, brownish-violet needles, having metallic reflex; it melts and decomposes at 205°. Hot hydrochloric acid does not liberate indigo from the substance; dilute caustic soda dissolves it, the deep red solution rapidly becoming brown when exposed to air. The solution in concentrated sulphuric acid is green, becoming blue when heated, a blue precipitate separating on dilution with water.

A blue substance is also precipitated when zinc dust is added to the alkaline solution, and quickly redissolves; the coloured liquid thus produced deposits a blue, amorphous precipitate on exposure to air. The compound, which is probably indigo-imide,



froms a green solution in concentrated sulphuric acid, becoming blue when heated; alkaline hydroxylamine regenerates indigo-oxime.



is obtained by heating indigo-oxime with zinc dust, anhydrous sodium acetate, and acetic anhydride; it separates from alcohol as a straw-coloured, crystalline powder, and melts at 176°, decomposing at 180°. Hot caustic soda yields a solution of indigo white. M. O. F.

Compounds of Antipyrine with Aldehydes. By GUSTAVE PATEIN (*Compt. rend.*, 1897, 125, 956—959. Compare Knorr, *Abstr.*, 1884, 1378; 1887, 601; and Schuftan, *Abstr.*, 1895, i, 482).—Knorr's compounds of antipyrine with aldehydes are most readily obtained by the following method. The aldehyde (1 mol.), antipyrine (2 mols.), and water are mixed together, and hydrochloric acid is added until solution is complete; after several hours, the crystalline mass which has formed is rendered alkaline with ammonia, the crystals separated, and re-

crystallised from dilute alcohol. The compounds thus obtained are true methane derivatives of the type $(C_{11}H_{11}N_2O)_2CH_2$ or $(C_{11}H_{11}N_2O)_2CH.R$.

Simple aldehydes do not yield derivatives in which the carbon of the aldehyde becomes united to the nitrogen of antipyrine. Chloral, on the other hand, yields no methane derivative, but a compound composed of one molecule of chloral with one of antipyrine.

J. J. S.

Constitution of the Safranines. V. By GEORGE F. JAUBERT (*Ber.*, 1898, 31, 1178—1189. Compare *Abstr.*, 1895, i, 527).—When a mixture of equal molecules of paraphenylenediamine and methylmetaphenylenediamine is oxidised with potassium dichromate, a methylamido-eurhodine, $NH_2 \cdot C_6H_3 \langle \begin{smallmatrix} N \\ \text{---} \end{smallmatrix} \rangle C_6H_3 \cdot NHMe$, is produced. If, however, methylmetatolylenediamine be employed, the product consists of *methyltolusafranine*, $NH_2 \cdot C_6H_3 \langle \begin{smallmatrix} N \\ \text{---} \\ NMe \end{smallmatrix} \rangle C_6H_2Me : NH$, which possesses all the properties of the safranines, forms a red solution in water, and dyes cotton on tannin in shades which are fast towards alkalis.

Ethyltolusafranine, $NH_2 \cdot C_6H_3 \langle \begin{smallmatrix} N \\ \text{---} \\ NEt \end{smallmatrix} \rangle C_6H_2Me : NH$, is prepared in a similar manner from ethylmetatolylenediamine [$Me : NH_2 : NH_2Et = 1 : 2 : 4$], and forms a green, crystalline *hydrochloride*. It readily yields a violet-blue diazo-compound, which reacts with β -naphthol to form a blue colouring matter. When it is diazotised in alcoholic solution, it yields *ethyltoluaposafranine*, $C_6H_4 \langle \begin{smallmatrix} N \\ \text{---} \\ NEt \end{smallmatrix} \rangle C_6H_2Me : NH$, which is a micro-crystalline powder with a bright green lustre. It forms a carmine-red solution in water, whilst the solution in hydrochloric acid is bluish-violet, and that in sulphuric acid green.

Trinitrometamidodiphenylamine [*trinitrophenylmetaphenylenediamine*], $NH_2 \cdot C_6H_4 \cdot NH \cdot C_6H_2(NO_2)_3$, is prepared by the action of picrylic chloride on metaphenylenediamine, and forms orange-red crystals, melting at $206\text{--}207^\circ$, which are readily soluble in alkalis. It can readily be converted into a diazo-compound, which yields an orange colouring matter with salicylic acid. When oxidised in presence of paraphenylenediamine hydrochloride, it yields *trinitrophenylsafranine*, $N \langle \begin{smallmatrix} C_6H_3(:NH) \\ \text{---} \\ C_6H_3(NH_2) \end{smallmatrix} \rangle N \cdot C_6H_2(NO_2)_3$, which produces very blue shades on cotton. The formation of a safranine in this way disproves the theory formulated by Nietzki (*Abstr.*, 1895, i, 624) to explain this reaction, since all the ortho-positions in one benzene ring are occupied.

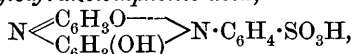
Trinitrophenylaposafranine, $N \langle \begin{smallmatrix} C_6H_3(:NH) \\ \text{---} \\ C_6H_4 \end{smallmatrix} \rangle N \cdot C_6H_2(NO_2)_3$, prepared in the usual manner, closely resembles ordinary aposafranine, but is precipitated by weaker alkalis. *Trinitrophenyldimethylmetaphenylenediamine* forms reddish-brown crystals, and when oxidised in the presence of paraphenylenediamine hydrochloride yields *trinitrodimethylphenosafranine*,

which crystallises in needles with a green lustre and closely resembles the non-methylated compound, yielding a blue-colouring matter when β -naphthol is added to its diazo-solution, and being converted into the corresponding *aposafranine* when diazotised in alcoholic solution.

Methylphenotolylaposafranine, $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_2\text{Me}(\text{:NH}) \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$, is formed by the replacement of the amido-group of the safranine T of commerce by hydrogen, and forms a green, crystalline *hydrochloride*.

Ethylsafranrol, $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_3\text{O} \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix} \text{NEt}$, can readily be obtained by the action of paranitrosophenol on ethylmetamidophenol in alkaline solution, and is a brown, crystalline powder, with a bright green surface lustre. The *sodium* salt, $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2\text{Na}$, crystallises readily, and is insoluble in concentrated alkalis.

Phenylsafranrolcarboxylic acid, $\text{O} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH}) \cdot \text{COOH}$, is prepared by oxidising a mixture of methahydroxydiphenylamine and paramidosalicylic acid. The *sodium* salt is a red, crystalline powder, which is freely soluble in water, whilst the free acid is a red, flocculent precipitate. *Phenylsafranrolsulphonic acid*,



formed by the action of methahydroxydiphenylaminesulphonic acid on paranitrosophenol, is a brown, crystalline powder with a green surface lustre. The *sodium* salt is readily soluble in water. *α -Naphthylsafranrol* and the corresponding β -derivative are green, crystalline powders, and correspond in properties with the other members of the class.

Ethylsafraninone, $\text{O} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \text{NEt} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NH}_2$, is formed by the action of ethylmetamidophenol on nitrosoaniline, and forms a red, crystalline *hydrochloride*, which dissolves in sulphuric acid to form a dirty-green coloured solution showing the characteristic dichroism of the rosinone derivatives.

Ethyltoluaposafranone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NEt} \end{smallmatrix} \text{C}_6\text{H}_2\text{MeO}$, formed when ethyltoluaposafranine is boiled with 75 per cent. sulphuric acid, crystallises in small, brown needles, which yield a dichroitic solution in sulphuric acid.

A. H.

Formation of Imido-1 : 2-diazole [1 : 2 : 3-Triazole] Derivatives from Aromatic Azimides and Ethereal Salts of Acetylenecarboxylic Acids. By ARTHUR MICHAEL, F. LUEHN, and HOWARD H. HIGBEE (*Amer. Chem. J.*, 1898, 20, 377—395).—*Methylic n-phenyl-1 : 2-imidodiazole*dicarboxylate [*methylic 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate*], $\text{N} \begin{smallmatrix} \text{NPh} \cdot \text{C} \cdot \text{COOMe} \\ \text{N} \text{---} \text{C} \cdot \text{COOMe} \end{smallmatrix}$, obtained by heating together equivalent amounts of phenylazimide and methylic acetylenedicarboxylate for 5 hours at 100°, crystallises from alcohol in white needles melting

at 127—128°. On hydrolysis, it yields the *free acid*, isomeric but not identical with Pechmann's *n*-phenylosotriazolecarboxylic acid (*Annalen*, 262, 311). It crystallises from water in long, prismatic needles melting and decomposing at 149—150°. The *silver* salt forms white needles sparingly soluble in cold water, and the *calcium* salt white, truncated prisms grouped together in star-like forms.

When the free acid is heated for some time at 150°, carbonic anhydride is given off from both carboxyl groups and *n*-phenyl-1:2-imidodiazole [1-phenyl-1:2:3-triazole], $\begin{matrix} \text{N}=\text{N} \\ | \\ \text{CH}:\text{CH} \end{matrix} \text{NPh}$, is formed as

white crystals melting at 55—56°; it is very stable towards oxidising agents, and its basic properties are so slightly developed that the hydrochloride only exists in solution, which, on evaporation, yields the original substance. The *platinochloride* forms long, prismatic needles.

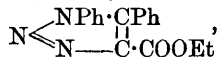
Methylic 1-paranitrophenyl-1:2:3-triazole-4:5-dicarboxylate, prepared by the action of nitrophenylazimide on methylic acetylenedicarboxylate, crystallises from alcohol in needles melting at 117—118°. The *free acid* separates from water in white plates and needles, the latter gradually passing over into the former on standing, and melts and decomposes at 162—163°. When reduced with stannous chloride in hydrochloric acid solution, the corresponding *amido-acid* is formed, separating from water in thick, prismatic crystals melting at 218—219° when rapidly heated. It is readily oxidised by potassium permanganate in alkaline solution, yielding 1:2:3-triazole-4:5-di-

carboxylic acid, $\text{N} \begin{matrix} \text{NH} \cdot \text{C} \cdot \text{COOH} \\ \diagdown \quad | \\ \text{N} \quad \text{C} \cdot \text{COOH} \end{matrix}$, identical with Bladin's acid (*Abstr.*,

1893, i, 375, 1894, i, 76); this forms prismatic crystals melting and evolving carbonic anhydride at 200—201°. The *potassium hydrogen* salt forms microscopic needles containing 1H₂O. During the oxidation, a second substance is produced in considerable amount; this separates from water in orange-red, granular crystals melting and decomposing at 328—330°, but was not further investigated.

1-Paranitrophenyl-1:2:3-triazole, obtained by heating nitrophenyl-1:2:3-triazoledicarboxylic acid at 160°, forms pale yellow, granular crystals melting at 203—204°. On reduction, it gives the corresponding *amido-derivative* crystallising in pearly flakes and melting at 138—139°.

Ethylic 1:5-diphenyl-1:2:3-triazole-4-carboxylate,



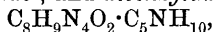
obtained by the interaction of phenylazimide and ethylic phenylpropionate, crystallises in needles melting at 134—135°. The *free acid* is a white, crystalline substance melting at 183°. The *silver* salt is a white, amorphous mass, and the *copper* salt forms groups of truncated slender prisms.

There can be no doubt that the addition of substituted azimides to ethereal salts of the acetylenedicarboxylic acids to form 1:2:3-triazole derivatives is a general reaction.

A. W. C.

Some Derivatives of Caffeine. By ALFRED EINHORN and EDUARD BAUMEISTER (*Ber.*, 1898, 31, 1138—1141).—Caffeinecarboxylamide, $\text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe}$
 $\text{CO} \cdot \text{NMe} \cdot \text{C} \begin{array}{c} \text{H} \\ | \\ \text{N} \end{array} \text{N} \begin{array}{c} \text{H} \\ | \\ \text{C} \end{array} \text{CO} \cdot \text{NH}_2$ (Gomberg, *Abstr.*, 1895, i, 628), reacts like caffeine itself (Maly and Andreasch, *Abstr.*, 1883, 1016) when it is boiled with aqueous caustic soda, and yields *caffeidinedicarboxylic acid*,
 $\text{COOH} \cdot \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe}$
 $\text{NHMe} \cdot \text{C} \begin{array}{c} \text{H} \\ | \\ \text{N} \end{array} \text{N} \begin{array}{c} \text{H} \\ | \\ \text{C} \end{array} \text{COOH} + \text{H}_2\text{O}$, which melts and decomposes at 141° ; when boiled with water, it loses carbonic anhydride, and forms caffeidine; its *sodium*, with $3\text{H}_2\text{O}$, and anhydrous *silver* salts were prepared and analysed.

Chlorocaffeine (1 mol.) reacts with secondary amines (2 mols.) when the two substances are heated together for 4—6 hours at 130 — 180° (compare Cramer, *Abstr.*, 1895, i, 116). *Piperidyl*, *diethylamido*-, *dipropylamido*-, *diamylamido*-, and *dibenzylamido*-caffeine,



&c., melt at 142° , 109° , 95° , 99.5° and 162° respectively. *Benzylamido*-caffeine, from chlorocaffeine, benzylamine, and alcohol at 180° , melts at 231° .
 C. F. B.

Cinchotine. By ZDENKO H. SKRAUP (*Annalen*, 1898, 300, 357—358. Compare O. Hesse, this vol., i, 388).—The author takes exception to certain statements made by Hesse (*loc. cit.*). He continues to call the base in question cinchotine, pointing out that the name hydrocinchonine, employed by Hesse, may give rise to confusion with the hydrocinchonines of Zorn, with none of which is the alkaloid identical.
 M. O. F.

Derivatives of Veratrine. By GEORGE B. FRANKFORTER (*Amer. Chem. J.*, 1898, 20, 358—373).—The veratrine employed was composed of microscopic, imperfect, granular crystals of a light grey colour; it is slightly soluble in water and very soluble in the ordinary organic solvents, separating as a light brown varnish, which, on stirring with water, changes to a granular, semi-crystalline mass melting at 146 — 148° . It has a peculiar, bitter, rasping taste producing numbness of the tongue if taken in small quantities: is a violent sternutatory, causing intense irritation of the nasal mucous membrane, and retards the action of the heart. It has a slightly alkaline reaction, which is intensified when dissolved in alcohol. The purified substance contains $1\text{H}_2\text{O}$, and one methoxy-group, a fact which has not previously been recorded. *Veratrine tetriodide* is produced when the alkaloid is triturated with an alcoholic solution of iodine and then allowed to remain with excess of iodine for some days, as a light red, crystalline powder melting at 129 — 130° . When dried at 110° to a constant weight, the *triiodide* is obtained as a dark brown, amorphous substance melting at 136 — 138° ; and when treated with dilute ammonia, it yields the *moniodide*, which separates from dilute alcohol as a fine, crystalline powder melting at 212 — 214° . When the *triiodide* is digested with strong ammonia, the whole of the iodine is removed, with production of a white, insoluble gelatinous substance melting at 189° , which is not identical with the free alkaloid.

Chloralhydroveratrine, $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{C}_{32}\text{H}_{48}\text{NO}_8)_2$, obtained by the action of chloral on the free alkaloid, is a creamy white, crystalline powder melting at 220° , and resembles veratrine in its physiological properties.

Veratrine methiodide, produced by the action of methylic iodide on the base, separates from water as an almost white, crystalline powder, melting at $210\text{--}212^\circ$ with apparent decomposition. When treated with potassium hydroxide or moist silver oxide, *veratrine methohydroxide* is obtained as a white, granular powder becoming brown when heated to $80\text{--}90^\circ$, but not finally melting until $188\text{--}190^\circ$; it is physiologically inactive. The *hydrochloride* is a light grey, very unstable, granular powder decomposing below 100° ; and the *aurochloride* is a beautiful, lemon yellow, crystalline powder melting at 149° .

Veratrine ethobromide is a light yellow, amorphous mass which readily decomposes; and the *allylic iodide* is a white, crystalline powder melting at $235\text{--}236^\circ$.
A. W. C.

Rotatory Power of Cocaine Hydrochloride. By HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 7, 59—61).—The author points out that the specific rotatory power of cocaine hydrochloride is often incorrectly stated to be $[\alpha]_D = -52.5^\circ$, and that this arises from a misinterpretation of Antrick's equation $[\alpha]_D = -[52.18 + 0.1588c]$ (compare Abstr., 1887, 506). In his determinations Antrick employed 40 per cent. alcohol as a solvent, since he found that, with water alone, a turbidity was produced. Five samples examined by the author, however, were probably of greater purity, since they dissolved in water, giving clear solutions, three of which gave $[\alpha]_D = -71.66$, whilst the remaining two gave $[\alpha]_D = -70.83$; each solution contained 2 grams of the hydrochloride per 100 c.c., and was examined at $14\text{--}16^\circ$. An aqueous solution of 2.712 grams per 100 c.c. of the hydrochloride which had been recrystallised from absolute alcohol, gave $[\alpha]_D = -71.94$, whilst 2 per cent. solutions in alcohol of the same concentration as that employed by Antrick gave the somewhat lower value of $[\alpha]_D = -69.43$, this again being decreased by increasing the concentration, so that for an 8 per cent. solution $[\alpha]_D = -69.15^\circ$.

That the author's values are higher than those of Antrick is probably due to his having used purer samples of the hydrochloride; no melting points are, however, given. He points out, in conclusion, that the rotatory power of cocaine hydrochloride is unaffected by heating its aqueous solution during 2 hours at 100° .

W. A. D.

Alkaloids of the Yellow Lupin (*Lupinus luteus*.) By HEINRICH RITTHAUSEN (*Chem. Zeit.*, 1897, 21, 718).—The alcoholic extract of yellow lupins, after being freed from alcohol, was mixed with an equal quantity of water and 1/10 of its weight of potassium hydroxide, and then extracted three times with light petroleum. The further separation of lupinine and lupinidine was effected by Baumert's method (Abstr., 1885, 177).
J. J. S.

Scopolamine. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, **236**, 9—11, 47—74. Compare Abstr., 1897, i, 385).—A reply to Hesse (Abstr., 1896, i, 655; and 1897, i, 132). According to the author, an almost inactive hydrobromide may be prepared from the scopolamine contained in scopolia root if the extract is made alkaline with potassium carbonate or sodium hydroxide; whilst the ordinary hydrobromide is obtained when a weak alkali such as sodium hydrogen carbonate is used. Similarly, the commercial hydrobromide yields an inactive scopolamine when the aqueous solution is made alkaline with sodium hydrogen carbonate; the same scopolamine is also obtained by the action of silver oxide, or of a small quantity of sodium hydroxide on the ordinary scopolamine, and is identical with Hesse's atroscine.

E. W. W.

Scopolamine and Scopoline. By WALTER LUBOLDT (*Arch. Pharm.*, 1898, **236**, 11—33. Compare Abstr., 1896, i, 514).—One hundred parts of water at 15° dissolve 1.4946 parts of scopolamine. The specific rotatory power of scopolamine in aqueous solution, $[\alpha]_D = -4^\circ 30'$, and in alcoholic solution $[\alpha]_D = -1^\circ 37'$. The product obtained by the action for a short time of concentrated sulphuric acid on scopolamine yields an *aurochloride*, $C_{34}H_{40}N_2O_7 \cdot 2HAuCl_4$, which crystallises from hot water in long needles and melts at 183—185° (uncorr.). Attempts to obtain the hydrochloride from the aurochloride by precipitating the gold with hydrogen sulphide and concentrating the filtrate, resulted only in the production of deliquescent needles which rapidly decomposed; from the solution, however, a *platinochloride*, $(C_{17}H_{19}NO_3)_2 \cdot H_2PtCl_6$, was obtained. The analogy between scopoline and tropine in regard to the products of oxidation and methylation is pointed out. According to the author, one of the atoms of oxygen contained in the molecule of scopoline probably occurs as a ketone group.

E. W. W.

Scopoleines. By WALTER LUBOLDT (*Arch. Pharm.*, 1898, **236**, 33—47. Compare Abstr., 1896, i, 396).—*Salicylscopoleine*, $C_{15}H_{17}NO_4$, prepared by melting commercial salicylide with scopoline, crystallises in slender, white needles, is slightly soluble in water, easily soluble in the usual organic solvents, and gives a violet coloration with ferric chloride. The hydrochloride, hydrobromide, sulphate, aurochloride, and platinochloride were prepared and analysed. *Phenylglycolylscopoleine* (homoscopolamine), $C_{16}H_{19}NO_4$, obtained by melting scopoline with mandelic anhydride, or by heating these substances dissolved in benzene at 140°, is a syrupy liquid which could not be crystallised; the aurochloride was prepared in the form of a resinous mass and analysed.

E. W. W.

Cactus Alkaloids. III. By ARTHUR HEFFTER (*Ber.*, 1898, **31**, 1193—1199. Compare Abstr., 1896, i, 267).—Pellotine not only contains two methoxy-groups, but a methyl group combined with nitrogen, and has the formula $C_{10}H_{10}O(OMe)_2NMe$. The *hydriodide* crystallises in small, yellowish prisms and is readily soluble in water.

The alkaloids of *Anhalonium Lewinii*, *Mezcaline hydrochloride*, crystallises in slender, white needles, whilst the *hydriodide* forms large, transparent plates, and the *aurochloride* long prisms. The *methiodide*,

$C_{11}H_{17}NO_3 \cdot MeI$, crystallises in colourless prisms melting at 174° , and yields a *methochloride*, the *platinochloride* of which crystallises in yellow needles. Mezcaline contains a methyl group united with nitrogen, and has the formula $C_7H_5(OMe)_3NMe$. It is converted by potassium permanganate into an *acid* which contains nitrogen, and crystallises in long, white needles melting at 169° .

Anhalonidine melts at 154° , and is optically inactive, the optical activity previously observed having been due to an impurity. The *hydrochloride*, *sulphate*, and *hydriodide* are all anhydrous and crystallise well, whilst the *aurochloride* melts at 152° . Anhalonidine, as previously stated, contains two methoxy-groups, but does not contain a methylimido-group or a hydroxyl group.

Anhalonine *hydriodide* forms yellowish needles, whilst the *aurochloride* is a heavy, microcrystalline powder. As a secondary base, anhalonine forms a *nitroso*-compound, $C_{12}H_{14}NO_3 \cdot NO$, which crystallises in colourless prisms melting at 59° . The base is converted by methylic iodide into *methylanhalonine hydriodide*, $C_{13}H_{17}NO_3 \cdot HI$, which forms spherical aggregates of white needles, whilst the corresponding *hydrochloride* crystallises in white needles, and forms a crystalline *aurochloride* and *platinochloride*. The free base crystallises from ether in thin plates, and unites with methylic iodide to form *methylanhalonine methiodide*, which melts at 210° and yields a *methochloride*, the *platinochloride* of which crystallises in needles.

Lophophorine has hitherto only been obtained as an oil, and in very small amount. The *hydrochloride*, $C_{12}H_{17}NO_3 \cdot HCl$, is optically inactive, and crystallises in microscopic needles. The base does not contain a methylimido-group, and is isomeric with methylanhalonine.

A. H.

What is Osborne's Diastase? By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1898, 31, 1127—1130).—A reply to Osborne (this vol., i, 286).

C. F. B.

Chemical Nature of the Amylolytic Ferments. By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1898, 31, 1130—1136).—*Diastase*.—When ammonium sulphate was added to an aqueous solution of impure diastase, a turbidity was produced when the solution contained about 50 per cent. of the sulphate and flakes of araban separated. More ammonium sulphate was then added until 60 per cent. was present; the precipitate then produced was a mixture of the pentosan with diastase. The second filtrate was saturated with ammonium sulphate; the precipitate now formed consisted of diastase only; 1 drop of a solution of it acted so vigorously on 0.1 gram of soluble starch, that after 2—3 minutes a blue colour could be obtained no longer with iodine. A specimen of this diastase was purified by dissolving it in water, separating it from ammonium sulphate by dialysis of the solution, and precipitating it with alcohol and ether; it contained 16.53 per cent. of nitrogen after this treatment. An aqueous solution of this diastase is not coagulated by boiling, even when acetic or hydrochloric acid in not too large amount has been added. It is precipitated by tannic acid, but the precipitate is soluble in very weak alkali, and this solu-

tion retains the power of hydrolysing starch. Diastase is a proteid, and is most nearly allied to the proteoses.

Takadiastase.—This substance, obtained by cultivating the fungus *Aspergillus oryzae* on wheat chaff, contains 44 per cent. of ash, chiefly phosphates; the rest consists of carbohydrates, proteids, and other substances. It was digested in water in the cold, the filtered solution was precipitated with alcohol, and the precipitate dissolved in water and treated much as above. A yellow substance was obtained eventually; it hydrolysed starch, and had the character of a proteid.

Invertin.—This substance, obtained from yeast, was separated from carbohydrates in the same way as takadiastase. One drop of its solution inverted 3 grams of cane-sugar in 3 minutes at 38°; it has the character of a proteid. C. F. B.

Oxyproteic Acid, a New Constituent of Urine. By STANISLAS BONDZYŃSKI and RUDOLF GOTTLIEB (*Chem. Centr.*, 1897, ii, 619—620; from *Centr. med. Wiss.*, 35, 578—580).—The barium salt of *oxyproteic acid*, $C_{43}H_{82}N_{14}O_{31}S$, is prepared from human or dogs' urine by adding 10 c.c. of 20 per cent. sulphuric acid to each litre of the concentrated syrupy urine and then 5 times the volume of alcohol, the filtrate is diluted with water, heated with barium hydroxide in excess, the barium removed by carbonic anhydride, the alcohol evaporated, the solution filtered, the filtrate concentrated, and then poured into 4 or 5 times its volume of alcohol. The flocculent precipitate so obtained is purified by dissolving in water and again precipitating with alcohol. In order to further purify the salt, the author makes use of the property which the acid possesses of being precipitated by mercuric nitrate or sulphate. The *barium* salt is a white, hygroscopic powder, is very soluble in water and insoluble in absolute alcohol. Salts of the alkalis and heavy metals could not be obtained in a pure state. Oxyproteic acid is obviously an oxidation product of albumin, and is probably analogous to the substance obtained by Maly by oxidising egg-albumin with permanganate, and to Schmiedeberg's oxyalbuminic acid. The acid, which was not obtained in the free state, neither gives the xantho-protein test nor the biuret reaction, and is not precipitated by phosphotungstic acid or by mercuric chloride. With Millon's reagent it gives a faint chamois-yellow coloration. The sulphur is not contained in the acid in a form which can easily be eliminated. No tyrosine is obtained by the action of sulphuric acid.

Mercuric nitrate precipitates from the urine of dogs which have been abundantly fed on flesh about 2·5 per cent. of the total nitrogen as oxyproteic acid, and the quantity of acid calculated from the barium salt amounts to about 10 grams per litre of urine. In human urine, 2—3 per cent. of the total nitrogen is in the form of this acid, and about 3—4 grams are eliminated in 24 hours. In cases of phosphorus poisoning in dogs, the amount of this acid increases considerably.

E. W. W.

So-called Oxyproteic Acid, a Constituent of Urine. By GUSTAV TÖPFFER (*Chem. Centr.*, 1897, ii, 956—957; from *Centr. med. Wiss.*, 35, 705—707).—Bondzyński and Gottlieb's oxyproteic acid

(preceding abstract) is identical with the substance prepared by the author (*Wien. klin. Woch.*, 1892, No. 3) from urine, by precipitating with phosphotungstic acid, then removing this acid with barium hydroxide, and finally precipitating the barium compound with alcohol, or by treating the urine with copper sulphate and alkali or baryta and then precipitating the barium salt with alcohol. According to the author, Bondzyński and Gottlieb have over-estimated the amount of this substance present in urine as their barium precipitate contained uric acid, creatinine and xanthine substances, and they are also wrong in stating that this substance [has been hitherto determined as urea, for by Mörner and Sjöqvist's method it is separated from the urea. This acid is precipitated by alcoholic mercuric chloride, but not by tannic acid or by potassium mercury iodide. E. W. W.

Sulphur in Proteids. By FRIEDRICH N. SCHULZ (*Zeit. physiol. Chem.*, 1898, 25, 16—35).—It is well known that the sulphur in proteids is partly removable by boiling with alkali, and partly not so. The proportion between these amounts is variously given by different observers. In the present research, the method used is a modification of Fleitmann's in which metallic zinc is added to the boiling alkali to prevent oxidation.

Treated in this way, thioacetic acid and thiourea yield the whole of their sulphur; thiosulphates, cystin, and cystein yield about half.

The following results (given in percentages) were obtained with proteids; in the case of the three first named, the proteid used was in the crystalline condition. With the exception of the egg-albumin, the preparations were made from horses' blood.

	Serum- albumin.	Egg- albumin.	Hæmo- globin.	Globin.	Serum- globulin.
Total sulphur (a)	1·89	1·18	0·43	0·42	1·38
Sulphur removable } by potash (b) }	1·28	0·49	0·19	0·2	0·63
a : b	3 : 2·03	2 : 0·83	2 : 0·88	2 : 0·95	2 : 0·91

W. D. H.

Cleavage Products of Proteids. I. Constituents of Witte's Peptone. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1898, 25, 152—164).—From Witte's 'peptone' pure protoalbumose may be prepared by precipitating the heteroalbumose by dialysing away the salts. From the filtrate, protoalbumose is precipitated as its copper compound, from which the copper is subsequently removed; it agrees in its properties with Kühne's protoalbumose. By lead acetate, it is broken up into two substances, one of which is similar to, or identical with, Meissner's meta-peptone or Kühne's acro-albumose; the second substance is present in smaller quantities and has yet to be investigated. After the removal of the protoalbumose, the last traces of which are got rid of by the addition of alcohol, saturation with ammonium sulphate precipitates the deuteroalbumose. This substance when pure is

free from the loosely combined sulphur which blackens lead acetate. In fact, the amount of sulphur altogether is so small (0.25 per cent.) that it may be due to contamination with impurities.

The 'so-called true peptone in Kühne's sense is regarded as non-existent, but as a mere residue of albumoses. This view has been previously expressed by Pekelharing (*Centr. f. Physiol.*, 7, 43).

W. D. H.

Action of Halogens on Proteids. By F. GOWLAND HOPKINS and STANISLAW N. PINKUS (*Ber.*, 1898, 31, 1311—1326).—Proteids in solutions of 0.6—5.0 per cent. strength absorb bromine readily at the ordinary temperature; no noticeable rise of temperature occurs, and the bromine is simply absorbed at first; only when excess has been added does a precipitate separate. In the case of protoalbumose and deutoalbumose, the temperature must not exceed 5° during bromination, otherwise the precipitate forms resinous lumps.

The reaction has been studied in greatest detail in the case of egg-albumin. This substance absorbs chlorine and iodine also; in the last case a temperature of 35—40° is necessary in order to produce a precipitate. The halogen acid formed can take no part in the reaction, for the same products are obtained with bromine and chlorine when potassium bromate or chlorate respectively is present, in which case no halogen acid can be formed. The original precipitate obtained with bromine contains 14.04 per cent. Br; after dialysis, 10.54. Three ways of purifying it were adopted, each way leading to a different product. (I) It was dissolved in 1 per cent. sodium carbonate solution, precipitated with 2 per cent. acetic acid, dialysed, washed with alcohol and ether, and dried under diminished pressure; it then formed a yellowish, amorphous powder; percentage of Br, 3.84—4.02 in different samples. (II) It was dissolved in hot alcohol and the solution run into cold ether, the precipitate was washed with ether and dried, when it formed a yellowish, amorphous powder containing Br, 10.69—10.98 per cent. (III) It was dissolved in alcohol, and bromine was added to this solution, which was then run into ether containing bromine; the precipitate was washed with ether and dried; it formed a reddish-white, amorphous powder, Br, 14.82—15.01. Any of the three products can be converted into the others by treating it in the way by which the latter were obtained. The mean percentage of bromine is quoted below, as also that of chlorine and iodine in products prepared by similar methods; it will be noticed that these numbers stand to each other roughly in the ratio of the atomic weights of the respective halogens, which indicates a similarity of constitution in the products.

	Chlorine.	Bromine.	Iodine.
Group I.	1.89 per cent.	3.92 per cent.	6.28 per cent.
Group II.	3.60 "	10.82 "	17.94 "
Group III.	6.07 "	14.91 "	—

These products in all cases form a horny mass, resembling dried white of egg, when they are dried slowly. They intumescence and carbonise at 160—200°, evolving halogen acid; they have an astringent, bitter taste; they do not dialyse, either from dilute alkaline or from

alcoholic solution ; they give the xanthoprotein and biuret reactions, but not Millon's or Adamkiewicz's ; they are pronounced acids, displacing carbonic acid, and they form insoluble salts with heavy metals ; when submitted to digestion, they yield substances which dialyse, have the character of peptones, and contain halogen ; the pancreatic digestion is rapid, but the peptic is slow, on account of the very slight solubility of the substances in acids.

As method III gave the most concordant results, it was adopted for further work. A number of proteids were treated by this method ; the results are tabulated below.

Protein.	Method of preparing the proteid.	Bromine.	Ash.
		Per cent.	Per cent.
Egg-albumin.....	Diluted with water	15·00	—
Cryst. „			
Fraction 1.....	According to Hofmeister	15·29	—
„ 2.....		16·48	—
„ 3.....		15·67	—
„ 4.....		12·64	—
„ 5.....		12·79	—
Serum-albumin 1.	Fractionated with $(\text{NH}_4)_2\text{SO}_4$, end fraction	12·61	—
2.	Salted out with $(\text{NH}_4)_2\text{SO}_4$	12·15	—
3.	According to Hammarsten	12·94	—
Serum-globulin 1.	Half-saturated with $(\text{NH}_4)_2\text{SO}_4$	14·03	—
2.	Saturated with MgSO_4	13·92	0·732
3.	Precipitated by diluting with water.	13·53	—
Casein	Dissolved in ammonia, precipitated with acetic acid	11·17	—
Protoalbumose	(Grübler)	16·30–17·12	—
Deuteroalbumose .	(Grübler)	17·63	—

C. F. B.

Production of a Mucinoid Substance by Bacteria. By ALBERT CHARRIN and ALEXANDRE DESGREZ (*Compt. rend.*, 1898, 126, 596—598).—When *Bacillus pyocyaneus* is cultivated in beef broth prepared in the usual way, the liquid often becomes viscous and yields a precipitate with alcohol, acetic acid, inorganic acids, sodium chloride, and magnesium sulphate, which is soluble in excess of the inorganic acids, and also dissolves in solutions of alkali hydroxides or carbonates. Its formation depends on the presence of beef extract, but has no relation to the production of pyocyanin. The precipitate produced by alcohol swells up in water and forms a pseudo-solution which can pass through a filter ; it contains sulphur, and in general characters resembles the mucinoids. A solution in dilute sodium carbonate solution when injected subcutaneously into the ear of a rabbit, produces diarrhœa and intramuscular hæmorrhagia, resulting in death. The formation by bacteria of a substance analogous to those produced by the cells of higher organisms is of special interest, and may play an important part in inflammations of the mucous membrane. Other bacteria seem to have the same power as *Bacillus pyocyaneus*.

C. H. B.

Organic Chemistry.

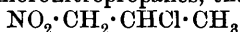
Some Aliphatic Nitro-compounds. By LOUIS HENRY (*Rec. Trav. Chim.*, 1898, 17, 1—26).—*Nitroethylic alcohol*, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, which cannot be obtained by the partial condensation of formaldehyde with nitromethane (compare this vol., i, 5), is conveniently prepared by dissolving ethylenic iodhydrin (86 grams) in three times its volume of ether, and leaving the solution in contact with silver nitrite (90 grams) during $1\frac{1}{2}$ hours at the ordinary temperature, the mixture finally being gently heated. A similar method was adopted by Meyer and Demuth (*Abstr.*, 1889, 360; 1890, 857), but on account of their employing impure ethylenic iodhydrin, they were unable to obtain a product having a definite boiling point. Nitroethylic alcohol is a colourless liquid, with a pungent odour and sharp taste, which boils at $119-120^\circ$ under a pressure of 35 mm., and at 194° , with slight decomposition, under a pressure of 765 mm.; it has a sp. gr. = 1.270 at 15° , its vapour density is 3.06 (calc. 3.14), and it does not solidify at -80° .

Nitropropylene, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NO}_2$, prepared by leaving a cooled ethereal solution of allylic bromide in contact with silver nitrite during $1\frac{1}{2}$ hours, and subsequently fractionating the product under reduced pressure, is a colourless, mobile liquid, with a pungent odour similar to that of allylic bromide, and a bitter taste; it has a sp. gr. = 1.051 at 21° , the vapour density is 3.08 (calc. 3.00), and it boils at $87-89^\circ$ under a pressure of 180 mm., and at $125-130^\circ$ under 760 mm.; in the latter case, an explosion generally occurs when the temperature reaches 130° . It is evident, from the properties given, that the nitropropylene described by Meyer and Askenasy (*Abstr.*, 1892, i, 1062) was highly impure.

αα-Chloronitroethane, prepared by passing chlorine into nitroethane dissolved in a slight excess of moderately concentrated caustic soda, or by adding the latter solution to carbon tetrachloride saturated with chlorine, is a colourless liquid which boils at $124-125^\circ$ (758 mm.), has a sp. gr. = 1.247 at 7.5° , a vapour density = 3.63 (calc. 3.78), and is soluble in alkalis; it condenses readily with formaldehyde, *ββ*-chloronitropropylic alcohol (this vol., i, 5) being obtained.

αβ-Chloronitroethane, $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{NO}_2$, formed together with its isomeride, chloroethylic nitrite, on heating ethylenic chloriodide with an excess of silver nitrite, is a colourless liquid which boils at 105° under a pressure of 72 mm., and at $173-174^\circ$ under the ordinary pressure; its sp. gr. = 1.405 at 7° , and its vapour density = 3.54 (calc. 3.78).

Of the five possible chloronitropropanes, the compounds



and $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NO}_2$ have already been described; the latter (*Abstr.*, 1897, i, 1), on being heated in a closed vessel with concentrated hydrochloric acid, yields hydroxylamine hydrochloride, and *β*-chloropropionic acid, which melts at $40-41^\circ$. The compound $\text{CH}_2\text{Me} \cdot \text{CHCl} \cdot \text{NO}_2$ is described in the following abstract, whilst that

having the formula $\text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{NO}_2$ is formed by the action of phosphorus pentachloride on the corresponding alcohol, $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NO}_2$; it is a colourless liquid which is insoluble in water, and boils at $170\text{--}174^\circ$ under a pressure of 155 mm., and at 94° under 46 mm.; its sp. gr. = 1.200 at 18° . β -Chloronitropropane, $\text{CH}_3\cdot\text{CMeCl}\cdot\text{NO}_2$, prepared by passing chlorine into secondary nitropropane dissolved in an equivalent quantity of aqueous potassium hydroxide, is a colourless liquid, with an agreeable odour, and is insoluble in water, but soluble in alcohol or ether; it boils at $133\text{--}134^\circ$ (758 mm.), has a vapour density = 4.12 (calc. 4.26), and a sp. gr. = 1.179 at 16° . As a consequence of its structure, it neither dissolves in alkalis nor condenses with aliphatic aldehydes.

Tetrachloronitropropane, $\text{CCl}_3\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{NO}_2$, prepared by the action of phosphorus pentachloride on the corresponding trichloronitroisopropyl alcohol, is a somewhat viscous liquid, with an odour resembling that of chloropicrin; it boils at $108\text{--}109^\circ$ under a pressure of 28 mm., at $199\text{--}200^\circ$ under 767 mm.; and has a sp. gr. = 1.580 at 11° , and a vapour density = 7.70 (calc. 7.84).

In conclusion, the author discusses the relation between the boiling point and structure of a number of halogen-substituted nitroparaffins.

W. A. D.

Derivatives of Primary Nitropropane. By J. PAUWELS (*Rec. Trav. Chim.*, 1898, 17, 27—49).—Primary nitropropane is best prepared (compare V. Meyer and Rilliet, this Journal, 1873, 261) by gradually adding normal propyl iodide to finely powdered silver nitrite suspended in ether, and finally heating for a short time on the water bath; it boils at $130\text{--}131^\circ$ under a pressure of 765 mm., and has a sp. gr. = 1.009 at 12° , and = 0.9999 at 16.5° . On mixing nitropropane (1 mol.) with an aqueous solution of formaldehyde (1 mol.) and adding a small piece of potassium carbonate, rapid combination takes place, *secondary nitro-normal butylic alcohol*, $\text{NO}_2\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{OH}$, being formed; this is a nearly colourless liquid, with a pungent odour and bitter taste; it boils at $127\text{--}130^\circ$ under 35 mm. pressure, has a sp. gr. = 1.1365 at 11.5° , and dissolves somewhat sparingly in water, but easily in alcohol, ether, and acetic acid. The vapour density is 2.60, instead of 4.11, owing probably to dissociation; the molecular weight, however, determined by the cryoscopic method, using water and acetic acid as solvents, is normal. The *sodium* derivative, $\text{NO}_2\cdot\text{CNaEt}\cdot\text{CH}_2\cdot\text{OH}$, of the alcohol is a white substance, insoluble in alcohol, but easily soluble in water; the *silver* salt, precipitated from the latter solution by silver nitrate, is a white powder soluble in ammonia; the *mercurous* salt is greyish-white, the *copper* salt green, and the *mercuric* and *ferric* salts red.

Since nitrobutylic alcohol contains the group $\cdot\text{CH}\cdot\text{NO}_2$, it readily condenses with formaldehyde (1 mol.) to form a *glycol* (2-methylol-2-nitro-1-butanol), $\text{NO}_2\cdot\text{CEt}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}_2\cdot\text{OH}$; the same product can also be obtained directly from nitropropane by condensation with 2 mols. of formaldehyde. It crystallises in white needles, melts at $57\text{--}58^\circ$, and is easily soluble in water, alcohol, and ether.

Nitrobutylic alcohol readily reacts with phosphorus pentachloride

to form *2-nitro-1-chlorobutane*, $\text{NO}_2 \cdot \text{CHEt} \cdot \text{CH}_2\text{Cl}$, a highly refractive, greenish-yellow liquid, which boils and partially decomposes at 190° (760 mm.), and has a sp. gr. = 1.165 at 21° , and a vapour density = 4.82 (calc. 4.75). *Nitrobutylic nitrate*, $\text{NO}_2 \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{NO}_3$, is a yellowish, somewhat viscous liquid, which has a sp. gr. = 1.242 at 15.5° . *Nitrobutylic acetate*, $\text{NO}_2 \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{OAc}$, boils at 130° under 35 mm. pressure, and has a sp. gr. = 1.0807 at 21° , and a vapour density = 6.19 (calc. 5.56).

Methyl-β-nitropropylcarbinol, $\text{NO}_2 \cdot \text{CHEt} \cdot \text{CHMe} \cdot \text{OH}$, obtained by the condensation of primary nitropropane with acetaldehyde, is a colourless liquid which is soluble in water, alcohol, and ether, and boils at 120° under 37 mm. pressure, and at 130° under a pressure of 54 mm.; it has a sp. gr. = 1.075 at 15.5° , and its vapour density is 4.34 (calc. 4.59).

αα-Chloronitropropane, $\text{NO}_2 \cdot \text{CHEtCl}$, prepared by passing chlorine through a solution of primary nitropropane in an equivalent quantity of aqueous caustic potash, is a colourless, mobile liquid which boils at $141\text{—}143^\circ$ (761 mm.), and has a sp. gr. = 1.205 at 15° , and a vapour density = 4.26 (calc. 4.27). It condenses readily with formaldehyde, forming *ββ-chloronitrobutylic alcohol*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CCl}(\text{NO}_2) \cdot \text{CH}_2\text{Me}$, a colourless, viscous liquid, which boils at $145\text{—}150^\circ$ under a pressure of 76 mm., has a sp. gr. = 1.229 at 15° , a vapour density = 5.13 (calc. 5.30), and is easily soluble in water, alcohol, and ether.

W. A. D.

Derivatives of Primary Nitroisobutane. By ANTOINE SHAW (*Rec. Trav. Chim.*, 1898, 17, 50—65).—When isobutylic iodide is left at the ordinary temperature with a slight excess of silver nitrite, a yield of 50—70 per cent. of the calculated quantity of primary nitroisobutane, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CHMe}_2$, is obtained; if, however, isobutylic bromide is employed, and the mixture heated, the yield is only 25—30 per cent. of the nitro-compound, 50 per cent. of isobutylic nitrite being formed. *Primary nitroisobutane* has a sp. gr. = 0.9870 at 15° ; on passing chlorine through its solution in aqueous caustic potash, it is converted into *αα-chloronitroisobutane*, $\text{NO}_2 \cdot \text{CHCl} \cdot \text{CHMe}_2$, a colourless mobile liquid, which boils at $151\text{—}152^\circ$ (750 mm.), has a sp. gr. = 1.147 at 13° , a vapour density = 4.58 (calc. 4.74), and is insoluble in water but easily soluble in ether and alcohol.

β-Nitroisobutylcarbinol, $\text{OH} \cdot \text{CH}_2 \cdot \text{CHPr}^s \cdot \text{NO}_2$, prepared by adding a small piece of potassium carbonate to a mixture of nitroisobutane and aqueous formaldehyde in molecular proportion, is a colourless liquid which boils at $138\text{—}139^\circ$ under a pressure of 38 mm., has a sp. gr. = 1.0966 at 13° , a vapour density = 4.12 (calc. 4.19), and is sparingly soluble in water, but easily in alcohol and ether. The *sodium* derivative, $\text{C}_6\text{H}_{10}\text{NO}_3\text{Na}$, forms white, deliquescent crystals, the *copper* derivative is green, the *mercurous* derivative greyish-black, and the *tin*, *silver*, and *barium* derivatives white. *αβ-Chloronitroisopentane*, $\text{CH}_2\text{Cl} \cdot \text{CHPr}^s \cdot \text{NO}_2$, prepared by the action of phosphorus pentachloride on *β-nitroisobutylcarbinol*, is a colourless liquid which is insoluble in water, soluble in alcohol and ether, boils at $163\text{—}170^\circ$ (758 mm.), and has a sp. gr. = 1.0416 at 15° , and a vapour density

= 5.09 (calc. 5.23). The acetate of β -nitroisobutylcarbinol, prepared by heating the latter with acetic anhydride, is a yellowish liquid which boils at 159–168° under a pressure of 38 mm., and has a sp. gr. = 1.0896 at 13°. The corresponding nitrate, $\text{NO}_2 \cdot \text{CHPr}^\beta \cdot \text{CH}_2 \cdot \text{NO}_3$, has a sp. gr. = 1.2373 at 15°.

A glycol, $\text{NO}_2 \cdot \text{CPr}^\beta (\text{CH}_2 \cdot \text{OH})_2$, is formed by the condensation of primary nitroisobutane with two molecules of formaldehyde, or, more conveniently, by condensing 1 mol. of the latter with β -nitroisobutylcarbinol; it crystallises from water, on slow evaporation, in white plates, and has a normal molecular weight in aqueous solution.

Methyl- α -nitroisobutylcarbinol, the condensation product of nitroisobutane with acetaldehyde, has already been described (this vol., i, 5).

$\beta\beta$ -Chloronitroisobutylcarbinol, $\text{OH} \cdot \text{CH}_2 \cdot \text{CClPr}^\beta \cdot \text{NO}_2$, prepared from $\alpha\alpha$ -chloronitroisobutane, $\text{NO}_2 \cdot \text{CHClPr}^\beta$, and formaldehyde, is a colourless liquid which boils at 153° under a pressure of 36 mm., has a sp. gr. = 1.2587 at 13°, a vapour density = 5.73 (calc. 5.77), and is insoluble in water, but soluble in alcohol and ether.

Attempts to prepare definite substances by condensing acetaldehyde with the nitroparaffins failed, products being obtained which could neither be crystallised nor distilled.

W. A. D.

Glycol and Aldol from Isobutaldehyde and Isovaleraldehyde.

By MORIZ LILIENFELD and SIEGFRIED TAUSS (*Monatsh.*, 1898, 19, 61–76. Compare next abstract).—The glycol, $\text{C}_9\text{H}_{20}\text{O}_2$, prepared according to Swoboda and Fosseck's directions (*Abstr.*, 1891, 31), is a crystalline substance melting at 79–80°, and boiling at 231–232° under atmospheric pressure, or 135° under a pressure of 16 mm. When oxidised with potassium permanganate in neutral solution, it yields a crystalline hydroxy-acid, $\text{C}_9\text{H}_{18}\text{O}_3$, melting at 69–70°, and probably also isopropyl isobutyl ketone. When the hydroxy-acid is oxidised with potassium permanganate in acid solution, or when heated with dilute sulphuric acid in sealed tubes for 8 hours at 140–150°, it is converted into a mixture of isobutyric and isovaleric acids. This supports Lieben's statement (*Monatsh.*, 1897, 18, 76, 85) that the substance is a primary secondary β -glycol, and not a disecundary glycol.

Swoboda and Fosseck (*loc. cit.*), by the action of sulphuric acid, obtained from the glycol two isomeric substances, the one of higher boiling point having a molecular weight twice as great as that of the one of lower boiling point. The authors find that oxidation of the latter with potassium permanganate or dichromate gives no satisfactory clue as to its nature, for working under very varying conditions they obtained only small amounts of volatile acids, acetone, and unchanged material.

The substance of higher boiling point is completely charred when heated in sealed tubes with sulphuric acid for 8 hours at 120–140°.

A mixture of isobutaldehyde and isovaleraldehyde, when treated with a saturated solution of potash, or when fused with potash, yields a thick syrupy liquid which cannot be distilled, as it at once splits up into a mixture of the two aldehydes, as it also does on treatment with sodium acetate. The substance, probably an aldol, is colourless, insoluble in water readily soluble in alcohol and ether, and does not

solidify when cooled in a freezing mixture. It reacts with hydroxylamine to form a very thick, colourless oil, probably the *oxime*, $C_9H_{19}NO$, boiling at $150-152^\circ$ under a pressure of 20 mm.

The aldol is not acted on by aluminium amalgam, but when treated with potassium permanganate, yields the hydroxy-acid, $C_9H_{18}O_3$, alluded to above.
A. W. C.

Aldol and Glycol from Isobutaldehyde and Acetaldehyde. By MORIZ LILIENFELD and SIEGFRIED TAUSS (*Monatsh.*, 1898, 19, 77—89. Compare preceding abstract).—The substance prepared by Swoboda and Fosseck (*Abstr.*, 1891, 31) by the condensation of acetaldehyde and isobutaldehyde and then termed methylisopropylethyleneglycol, is now shown to be a primary secondary β -glycol. The condensation, which does not take place readily, yields from 2—10 per cent. of the *glycol*, $C_6H_{14}O_2$, as a thick liquid boiling at 118° under a pressure of 21 mm. or 208° (uncorr.) at atmospheric pressure. It does not solidify in a freezing mixture, although Fosseck expressly states that it does solidify when cooled to 0° . By the action of aqueous potash on a mixture of acetaldehyde and isobutaldehyde, an *aldol*, $C_6H_{12}O_2$, is formed as a thick, colourless liquid, with pleasant odour and bitter taste, boiling at $88-90^\circ$ under a pressure of 22 mm.; it could not be made to solidify. When heated with sodium acetate in sealed tubes at $80-90^\circ$ for some hours, it is converted into isobutaldehyde and crotonaldehyde. It yields an *oxime* as a colourless, thick liquid with a peculiar and characteristic odour; it boils at $137-139^\circ$ under a pressure of 19 mm., and, when heated with acetic anhydride, yields the *monacetyl* derivative of the corresponding *nitrile* as a colourless liquid boiling at 105° under a pressure of 16 mm. When hydrolysed with concentrated potash, a *hydroxy-acid*, $C_6H_{12}O_3$, is produced as a yellowish oil with a strong acid reaction.

The aldol is readily oxidised by potassium permanganate, giving the same hydroxy-acid, and also methyl isopropyl ketone; on reduction with aluminium amalgam, the glycol, $C_6H_{14}O_2$, is produced. When the glycol is treated with dilute or concentrated sulphuric acid, an oil smelling like camphor is obtained, which, on distillation, yields two fractions boiling at $103-105^\circ$ and 210° . The substance of lower boiling point is probably trimethyltrimethylene oxide, but no definite results have so far been arrived at.
A. W. C.

Glycerol Compounds of Copper with Alkali Metals. By FRIEDRICH BULLNHEIMER (*Ber.*, 1898, 31, 1453—1457).—A compound, $2C_3H_5O_3CuNa + EtOH + 9H_2O$, was prepared by mixing 5 grams of copper hydroxide, 15 c.c. of water, 2.5—3 grams of glycerol, and 3 grams of pure caustic soda, allowing the mixture to remain in a closed vessel till a solution had been formed, adding 50 c.c. of alcohol (96 per cent.), filtering, adding more alcohol (about 30 c.c.) until a turbidity appeared, and then allowing to remain. The compound crystallises in small but long prisms, blue in colour; at 100° , under diminished pressure, it loses alcohol and water, $2C_3H_5O_3CuNa + 3H_2O$ remaining (the substance analysed was dried under diminished pressure, but in the absence of a drying agent); it absorbs carbonic anhydride from the air, copper carbonate being formed.

Another compound, $C_3H_5O_3CuNa + 3H_2O$, was obtained by dissolving 3 grams of copper nitrate in 1 gram of glycerol and 2 c.c. of water, diluting to 100 c.c. with alcohol (96 per cent.), warming to 70° , adding 5 c.c. of a solution of 2.5 grams of caustic soda in water, shaking for a little while, pouring off the hot, nearly clear deep blue solution from the dark green, slimy deposit, and allowing it to remain in a closed vessel. It crystallises in blue, hexagonal plates, with an angle of about 60° ; it absorbs carbonic anhydride and water from the air; its solution in water deposits cupric oxide when boiled.

A compound, $C_3H_5O_3CuLi + 6H_2O$, was obtained by dissolving 4 grams of lithium hydroxide in a hot mixture of 60 c.c. water and 60 c.c. alcohol (96 per cent.), adding a solution, saturated at 60° , of copper acetate in 25 c.c. water, 50 c.c. alcohol, and 2 grams of glycerol, filtering the hot solution, diluting it with 200 c.c. alcohol and 60–80 c.c. ether, and allowing it to remain at 0° . The compound crystallises in elongated, hexagonal plates.

C. F. B.

The Glucoses formed from Chagual Gum. By ERNST WINTERSTEIN (*Ber.*, 1898, 31, 1571–1573).—Chagual gum, the product of a monocotyledonous plant, dissolves in water to a large extent; the solution is only feebly dextrorotatory, and does not reduce Fehling's solution. When oxidised with nitric acid of sp. gr. = 1.15, the gum yields 21 per cent. of mucic acid; when distilled with 12 per cent. hydrochloric acid, it yields 24 per cent. of furfuraldehyde; it must, then, be capable of yielding 28.5 per cent. of galactose, and 45 per cent. of pentose. The best yield of carbohydrates was obtained by boiling the gum for 4–5 hours with 5 per cent. sulphuric acid in a reflux apparatus; the portion of the product more soluble in strong alcohol was xylose, the less soluble portion appeared to be a mixture of *i*-galactose with a little *d*-galactose.

C. F. B.

Double Salts containing Selenium. By JAMES F. NORRIS (*Amer. Chem. J.*, 1898, 20, 490–508).—Selenium tetrachloride is decomposed by water even in presence of strong hydrochloric acid, and is incapable of forming double salts with ammonium chloride. Muthmann and Schäfer have shown that the only double compound obtainable with selenium and ammonium chloride has the composition $2SeO_2 \cdot NH_4Cl + 2H_2O$ (*Abstr.*, 1893, ii, 318). In the case of double salts containing dimethylamine and trimethylamine, the author finds that the introduction of the alkyl groups has a marked influence on the stability of the selenium haloids, and that salts containing $SeOCl_2$ are capable of existence.

Salts with Trimethylamine.—The salt $SeOCl_2 \cdot NMe_3 \cdot HCl$, prepared by mixing a strong hydrochloric acid solution of trimethylamine with excess of selenium tetrachloride, can be obtained in well-defined, colourless, monoclinic plates; it is hygroscopic and very soluble in water, hydrochloric acid, and alcohol.

The salt $SeOCl_2 \cdot SeO_2 \cdot 2NMe_3 \cdot HCl + H_2O$, obtained from the preceding salt by recrystallising it from alcohol and ether containing no hydrochloric acid, forms colourless, semi-transparent plates.

In making these chlorides, selenium dioxide and hydrochloric acid may be employed instead of the tetrachloride.

The salt $\text{SeBr}_4, \text{SeOBr}_2, 2\text{NMe}_3, \text{HBr}$, obtained by mixing selenium tetrabromide with trimethylamine hydrobromide, dissolved in dilute hydrobromic acid and evaporating the solution, crystallises in long, red needles or in deep red orthorhombic crystals; it is stable in a dry atmosphere.

The salt $\text{SeBr}_4, 2\text{NMe}_3, \text{HBr}$ is obtained when a solution containing an excess of trimethylamine hydrobromide is evaporated, rejecting the crystals first formed; it forms large, red octahedra. The corresponding double haloids of ammonium, potassium, and rubidium with selenium bromide also crystallise in octahedra. The first crop referred to above also contains greenish-brown needles, which are probably those of another double bromide which has not hitherto been obtained pure.

The salt $\text{SeBr}_4, 2(\text{NMe}_3, \text{HBr}_2)$ crystallises in stout, dark-red needles when bromine is added to a hot saturated solution containing 1 molecular proportion of selenium tetrabromide and two of trimethylamine hydrobromide in dilute hydrobromic acid. Two atomic proportions of bromine are liberated when it is dissolved in water.

The salt $\text{SeBr}_4, 2(\text{NMe}_3, \text{HBr}_2), \text{NMe}_3$ separates in red crystals when a solution containing selenium tetrabromide, bromine, and a large excess of trimethylamine hydrobromide is allowed to evaporate; it also loses bromine when dissolved in water.

Salts with Dimethylamine.—The salt $2\text{SeOCl}_2, 3\text{NHMe}_2, \text{HCl}$ is deposited in monoclinic crystals from a solution containing 2 molecular proportions of selenium tetrachloride (or selenium dioxide) and one of dimethylamine hydrochloride in strong hydrochloric acid; it is deliquescent, and dissolves readily in water, alcohol, and hydrochloric acid.

The salt $\text{SeO}_2, \text{NHMe}_2, \text{HCl}$ is obtained in stout, colourless prisms when a solution of the preceding salt is crystallised from alcohol and ether. Dimethylamine resembles ammonia in forming a double salt containing selenium dioxide; the corresponding trimethylamine salt does not exist.

The salt $2\text{SeBr}_4, \text{SeBr}, 3\text{NHMe}_2, \text{HBr}$ crystallises in dark-brown, diamond-shaped plates when a concentrated hydrobromic acid solution containing dimethylamine hydrobromide and excess of selenium tetrabromide is evaporated. The salt is decomposed by water with the liberation of selenium, and probably contains the elements of selenium monobromide, which is similarly decomposed in aqueous solutions.

The salt $\text{SeBr}_4, 2(\text{NHMe}_2, \text{HBr})$ crystallises in bright red, prismatic needles when a dilute hydrobromic acid solution of selenium tetrabromide and dimethylamine hydrobromide is evaporated. This compound can be obtained in monoclinic or triclinic prisms, whereas the other bromides of the type $\text{SeBr}_4, 2\text{MBr}$, containing potassium, rubidium, ammonium, and trimethylammonium, crystallise in octahedra.

A third bromide crystallising like the trimethylamine compound in green needles is produced, but cannot be purified.

The salt $\text{SeBr}_4, 2(\text{NHMe}_2, \text{HBr}_2)$, prepared like the corresponding trimethylamine double salt, crystallises in dark red needles.

The salt $\text{SeBr}_4, 2(\text{NHMe}_2, \text{HBr}_2), \text{NHMe}_2, \text{HBr}$ crystallises in deep brown prisms on adding bromine to a saturated solution of selenium tetrabromide and excess of dimethylamine hydrobromide in strong hydrobromic acid.

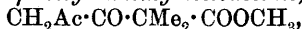
G. T. M.

Preparation of a Synthetic Methylheptenone. By GEORGES LESER (*Bull. Soc. Chim.*, 1897, [iii], 17, 108—110).—Tiemann and Krüger (*Abstr.*, 1895, i, 645) were unable to isolate the methylheptenone, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{Me}$, obtained by Barbier and Bouveault (*Abstr.*, 1894, i, 224) by the condensation of isovaleraldehyde with acetone, and stated that the principal product of the reaction was di-isovaleraldehyde, boiling at 190° . The author finds, however, that if a mixture of isovaleraldehyde (1 part), acetone (1 part), sodium hydroxide solution (1:10; 1 part), and water (3 parts) is kept in constant agitation for about 12 hours, and the supernatant liquid subjected to repeated fractional distillation, the methylheptenone boiling at 180° (corr.) is easily obtained in quantity, whilst the portion boiling above 180° is relatively small in amount. N. L.

Action of Sodium on Ethylic Dimethylacetoacetate. By MAX CONRAD and RICHARD GAST (*Ber.*, 1898, 31, 1339—1344).—Ethylic malonate containing a minute quantity of dry hydrogen chloride in solution has little or no action on metallic sodium; it is suggested that the reason why ethylic malonate dried by silicon tetrachloride does not react with sodium (Nef, *Abstr.*, 1892, 140) is the presence of small quantities of hydrogen chloride.

Sodium does not react with methylic dimethylacetoacetate at the ordinary temperature, but at 95 — 100° the metal slowly dissolves, and at 115 — 125° the reaction proceeds vigorously and hydrogen is evolved.

When methylic dimethylacetoacetate (86 grams) is heated in a reflux apparatus at 110 — 120° with metallic sodium (6.9 grams), and the heating continued for 2 hours, then neutralised with acid and precipitated with water, and the ethereal layer fractionally distilled, the portion distilling below 100° consists chiefly of methylic isobutyrate. About 30 grams passes over at 220 — 240° , and the greater portion of this consists of *ethylic- γ -acetyldimethylacetoacetate*,



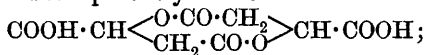
boiling at 228 — 232° ; it is a yellowish oil, miscible with alcohol, ether, or benzene in all proportions, and gives an intense red coloration with ferric chloride. Its *sodium* derivative, $\text{CHNaAc} \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{COOMe}$, is obtained as a white, crystalline deposit when the ethereal salt is shaken with a solution of sodium methoxide in ether and methylic alcohol. The *copper* derivative, obtained by shaking a solution of the methylic salt in light petroleum with a solution of copper acetate, forms a pale blue, crystalline precipitate melting at 109° . The *monoxime*, obtained by heating a methyl alcoholic solution of the methylic salt with water, sodium carbonate, and sufficient hydroxylamine hydrochloride to yield the dioxime, crystallises from methylic alcohol in colourless crystals melting at 115° . No dioxime could be obtained, a fact which appears to indicate that the methylic salt contains but one carbonyl group. When the ethereal salt is heated at 120° for several hours with dilute hydrochloric acid, it is decomposed into carbonic anhydride, methylic alcohol, and *acetylisobutyrylmethane*, $\text{CH}_2\text{Ac} \cdot \text{CO} \cdot \text{CHMe}_2$, which boils at 160 — 170° , and yields a *copper* derivative crystallising from its hot methyl alcoholic solution in glistening, blue needles melting at 171° . Barium hydroxide induces a similar hydrolysis. When

10 grams of methylic γ -acetyldimethylacetoacetate or methylic α -dimethyltriacetate (Collie) is mixed with 25 c.c. of concentrated ammonia, and the mixture kept first in a closed vessel for several hours and then heated on the water bath, about 6 grams of *trimethyl-diketotetrahydropyridine*, $\text{CO} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CH} : \text{CMe} \end{smallmatrix} \text{NH}$, or *trimethyl- α -hydroxy- γ -ketodihydropyridine*, $\text{CO} \begin{smallmatrix} \text{CMe}_2 \cdot \text{C(OH)} \\ \text{CH} = \text{CMe} \end{smallmatrix} \text{N}$, is obtained; this crystallises from hot ethylic acetate or benzene in well-developed prisms melting at 140° , but is readily soluble in hot water or in alcohol, but only sparingly in ether. When treated with an excess of phenylhydrazine, it yields a *monophenylhydrazone* melting at 155° . J. J. S.

Action of Ammonia on Ethylic Methylglyoximecarboxylate. By KARL ERBSTEIN (*Arch. Pharm.*, 1898, 236, 150—152).—By the action of ammonia on ethylic methylglyoximecarboxylate, the amide of methylglyoximecarboxylic acid, $\text{NOH} : \text{CMe} \cdot \text{C}(\text{NOH}) \cdot \text{CO} \cdot \text{NH}_2$, and varying amounts of other compounds are formed according to the conditions of the experiment. In one case, a neutral substance, $\text{C}_3\text{H}_6\text{N}_2\text{O}_2$, was obtained, which decomposed at 181° , crystallised from hot water, and when heated with strong sodium hydroxide solution evolved ammonia and formed an acid melting at 135 — 140° . This acid the author regards as a stereoisomeride of oximidopropionic acid. When 1 part of ethylic methylglyoximecarboxylate is heated with 8 parts of concentrated ammonia at 100° , the amide of methylglyoximecarboxylic acid, the amide of methylfurazancarboxylic acid, $\text{O} \begin{smallmatrix} \text{N} : \text{CMe} \\ \text{N} : \text{C} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, methylglyoxime, oximidomethyloxazolone, and a volatile acid with an odour like acetic acid are formed. The amide of methylglyoximecarboxylic acid crystallises from hot water in colourless prisms, or plates, sinters at 180° , and decomposes and intumesces at 183° ; it is easily soluble in alcohol, acetone, and hot water, sparingly so in ether, chloroform, and benzene, and dissolves in cold sodium hydroxide solution with liberation of ammonia; with ferric chloride in aqueous solution, it gives a yellowish-red coloration, and by the action of warm hydrochloric acid it decomposes into oxalic acid and oximidomethyloxazolone. By the action of boiling sodium hydroxide solution, oximidopropionic acid (m. p. 177°), and methylloximido-oxazolone are formed, and when heated with ammonia it yields the amide of methylfurazancarboxylic acid; the latter crystallises in lustrous needles, melts at 124° , and is easily soluble in alcohol, chloroform, and hot water; when boiled for a short time with sodium hydroxide solution, it yields ammonia and Wolff's methylfurazancarboxylic acid, $\text{C}_4\text{H}_4\text{N}_2\text{O}_3 + \text{H}_2\text{O}$, whilst by the prolonged action of the alkali, oximidopropionic acid is obtained. E. W. W.

Malic Acid from Crassulaceæ. By J. H. ABERSON (*Ber.*, 1898, 31, 1432—1449).—The acid was prepared chiefly from *Echeveria secunda glauca* and *Sedum purpurescens* (*Bryophyllum calycinum* yields more, namely, about 0.23 per cent. of the leaves, but is less easily

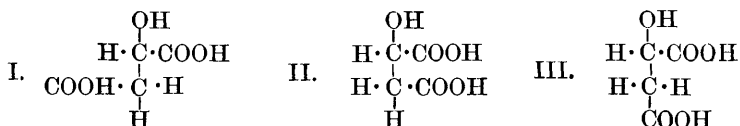
obtainable) by extraction with boiling water, precipitation of the lead salt, and decomposition of this with hydrogen sulphide. The residue left on evaporation of the aqueous solution, when dried at 110° until constant in weight, has the composition $C_8H_8O_8$; it represents an anhydride of the acid, for the salts prepared from it are derived from a dibasic acid, $C_4H_6O_5$. The *calcium hydrogen* salt is usually amorphous, but was once obtained in regular octahedra with $6H_2O$; the corresponding salt of ordinary malic acid crystallises in rhombic octahedra. The *barium* salt is anhydrous, whereas ordinary barium malate crystallises with $1H_2O$. The *silver* salt is anhydrous, whereas ordinary silver malate contains $5H_2O$. The *lead* salt crystallises with $3H_2O$. No ammonium hydrogen salt could be prepared, whereas ordinary malic acid forms a well crystallised salt of this composition. The *dimethylic* salt was prepared from the anhydride and methylic alcohol by Anschütz's method; it distils at 162° under 25 mm. pressure; after this has passed over, a second product is obtained, to which reference will be made later. The dimethylic salt is converted by alcoholic ammonia at 100° into the *amide*, which melts at $174-178^{\circ}$. The formula assigned to the acid above was confirmed by determinations of the freezing point of aqueous solutions, and of the electrical conductivity of the sodium salt. The acid has the specific rotation $[\alpha]_D = +9.8^{\circ}$ at 15° in aqueous solution, that of ordinary malic acid being -5.8° ; the anhydride has $[\alpha]_D = -39.5^{\circ}$ in acetone solution, and it is found that concentrated solutions of the acid in water are increasingly lævorotatory, doubtless owing to the formation of anhydride. The potassium and sodium salts are lævorotatory. When the acid is distilled under diminished pressure, a little fumaric acid and some maleic anhydride distil over, but the bulk passes over as the anhydride of the acid itself; a little carbonic anhydride and oxide, and some aldehyde, are formed in addition. Much the same thing happens under ordinary pressure, except that a large part of the acid remains behind in the flask. When ordinary malic acid is distilled under diminished pressure, fumaric acid and maleic anhydride are formed in almost theoretical amount; no gas is evolved. It has been said that the acid from *Crassulaceæ*, unlike ordinary malic acid from mountain-ash berries, forms an anhydride. This anhydride is itself a dibasic acid, and has probably the constitution



it may be called *malide*. Its *dimethylic* salt, boiling at 210° under about 25 mm. pressure, and melting at 102° , distils over finally in the preparation of the dimethylic salt mentioned above; its *diethylic* salt, boiling at $245-250^{\circ}$ under 30 mm. pressure, is the sole product of the action of ethylic alcohol on the anhydride. Boiling with potash converts the malide into the malic acid; heating with water for a short time only carries this change to the half-way stage, the product yielding a silver salt, $C_8H_7O_9Ag_3$. This same silver salt is obtained by the action of aqueous silver nitrate on the malide; alcoholic silver nitrate, mixed with the calculated quantity of alcoholic ammonia, forms the true silver salt of the malide, $C_8H_6O_8Ag_2$. The diethylic

salt is completely converted into the malic acid when boiled for 10 hours with water. The analogy between this malic acid and *d*-lactic acid is striking.

This malic acid is reduced to succinic acid by hydriodic acid and phosphorus at 100°; further, it is a dibasic acid, and, being optically active, it must contain an asymmetric carbon atom, so that its formula must be $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$. There are three possible configurations of this formula, which may be assumed to possess a certain degree of stability:



Of these, I represents ordinary malic acid, which is mostly converted into fumaric acid when distilled, and II may be regarded as an unstable form momentarily assumed by a part of this acid before its conversion into maleic anhydride. The acid from the *Crassulaceae* must have the configuration III, which must therefore be regarded as no less stable than I, contrary to Wislicenus' views, according to which I, being the more "favoured" configuration, ought to be the only stable one.

C. F. B.

Reciprocal Transformation of Tartaric, Racemic, and Mesotartaric Acids. By ARNOLD FREDERICK HOLLEMAN (*Rec. Trav. Chim.*, 1898, 17, 66—85).—The difference in micro-crystalline character of the calcium salts of the three acids renders it possible to detect a trace of any one of them in presence of the other two. For quantitative separation the following process gives good results: the aqueous solution of the free acids is evaporated on the water-bath, until crystallisation commences, and then left during 24 hours; the racemic acid separates quantitatively, and is carefully drained and weighed. The mother liquor is diluted to a suitable volume (20 c.c.), and half of the latter exactly neutralised by caustic potash; on adding the unneutralised portion and leaving overnight, a quantitative separation of potassium hydrogen tartrate is obtained, which is washed with very little water, and weighed. By neutralising the filtrate with ammonia, slightly acidifying with acetic acid, boiling and adding calcium chloride, the mesotartaric acid is completely precipitated, and, after 24 hours, can be collected and weighed as calcium salt.

Employing this method, the author has studied the behaviour of pure tartaric, racemic, and mesotartaric acids (in each case 6 grams being taken), when heated with 4 c.c. of normal hydrochloric acid in sealed tubes at fixed temperatures between 109° and 155°.

From tartaric acid, at temperatures below 140°, mesotartaric acid is almost the sole product, traces only of racemic acid being formed; after heating 42 hours at 155°, however, the amount of the latter is 6·7 per cent., that of the former being 18 per cent.; considerable decomposition, however, occurs between 140° and 155°, which is shown by the great increase in pressure in the tubes.

Whilst 19 per cent. of mesotartaric acid is formed on heating racemic acid with normal hydrochloric acid during 100 hours at 140° , 10 per cent. only of racemic acid is obtained from mesotartaric acid under the same conditions; these facts explain the preponderance of mesotartaric acid in the product obtained from tartaric acid at 140° .

Meissner has stated (Abstr., 1897, i, 460) that small quantities only of mesotartaric acid are formed on treating tartaric acid for 8 hours with boiling alkali; the author finds, however, that under these circumstances 24 per cent. of the former acid is obtained, the yield being a maximum (31.5 per cent.) after two hours heating; so that this affords a method of preparing mesotartaric acid much more rapid than that proposed by Jungfleisch.

In discussing the theoretical side of the question, the author points out that, since di-isobutylic tartrate is not changed when heated for 72 hours at 200° , the reciprocal transformation of the acids dealt with depends solely on the hydrogen ions. The fact that mesotartaric acid is formed with greater ease than racemic acid from tartaric acid, is explained by assuming that, whereas the production of the former involves only one of the asymmetric carbon atoms, that of the latter is dependent on both of them being changed. W. A. D.

Conversion of Gluconic Acid into *d*-Arabinose. By OTTO RUFF (*Ber.*, 1898, 31, 1573—1577. Compare Cross, Bevan and Smith, *Trans.*, 1898, 463).—Calcium gluconate was oxidised in two ways: with bromine in the presence of lead carbonate and water at the ordinary temperature, when the oxidation is complete in 10 hours if the mixture is shaken frequently; and also with hydrogen peroxide (containing 1.2 per cent. of oxygen) and a little basic ferric acetate solution at 38° , the mixture being allowed to stand for 3 days and the excess of peroxide then removed by treatment with freshly precipitated manganese dioxide. In both cases, about two-thirds of an atom of oxygen was used per 1 mol. of the gluconate; the product was treated with alcoholic hydroxylamine, and *d*-arabinoseoxime was obtained eventually; this melts at 138 — 139° , and shows multirotation, reaching finally the value $[\alpha]_D = -13.23^{\circ}$ at 20° in 8 per cent. aqueous solution; when heated with phenylhydrazine and acetic acid, it yields an *osazone* melting at 159 — 160° when crystallised from water, and at 162 — 163° when first crystallised from benzene; with parabromophenylhydrazine it yields a *bromosazone* melting at 163° .

Calcium gluconate (1 mol.) can be oxidised simply by basic ferric acetate (1 mol.) in sunlight; the products are arabinose and a little formaldehyde. C. F. B.

Action of Hydriodic Acid on Aromatic Bromine Derivatives. By JOSEF HERZIG (*Monatsh.*, 1898, 19, 90—94).—When dibromodiethylorcinol or tribromodihydroxybenzoic acid (m. p. 187 — 189°) is heated with hydriodic acid of sp. gr. = 1.7, the bromine is completely removed, showing that when two hydroxyl groups are present in the meta-position, the third group can be methyl or carboxyl without the nature of the reaction suffering any change.

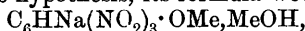
With tribromometahydroxybenzoic acid and hydriodic acid, the reaction is slower, the whole of the halogen not being removed until after

heating for 18 hours, instead of from 2 to 3 hours as in the previous cases. The conclusion might be drawn that this reaction depends only on the symmetrical position of the three bromine atoms, the presence of two or three substituents in the meta-position being only of secondary importance; this argument, however, does not appear to hold good, for symmetrical tribromobenzoic acid was heated for 30 hours with hydriodic acid without suffering decomposition.

Orthobromotoluene, and ortho- and para-bromobenzoic acids are not affected by boiling with hydriodic acid.

The author has already shown (Abstr., 1886, 232) that brominated phloroglucinol derivatives give up their bromine when treated with dilute alkalis, and it seemed possible that this and the action of hydriodic acid might be corresponding reactions. Experiment, however, does not support this belief, for tribromodihydroxybenzoic acid does not give up bromine on treatment with dilute alkalis. A. W. C.

Coloured Compounds obtained from Sodium Alkyl oxides and Picryl Chloride. By CHARLES LORING JACKSON and W. F. BOOS (*Amer. Chem. J.*, 1898, 20, 444—455. Compare Abstr., 1897, i, 332). —The exact constitution of the compounds produced in this reaction is still unknown. Empirically they consist of a molecule of an alkyl picrate combined with 1 molecule of sodium alkyl oxide. The authors point out that the experimental results are opposed to the constitution suggested by V. Meyer (Abstr., 1895, i, 95) in which one hydrogen atom of the benzene nucleus is represented as being replaced by sodium. The *methylic* compound, $C_6H_2(NO_2)_3 \cdot OMe, MeONa$, produced by the action of excess of sodium methoxide on picryl chloride in methylic alcohol, separates in the form of scarlet needles, decomposes at 165° , and explodes violently when heated to higher temperatures. Water or methylic alcohol slowly decomposes it, and acids cause immediate decomposition, trinitranisole being produced in both cases. According to Meyer's hypothesis, its formula would be



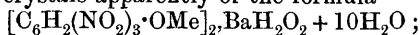
and it should therefore contain methylic alcohol of crystallisation, but the substance suffers no loss in weight when heated at 130° , and it has not been found possible to obtain the compound $CHNa(NO_2)_3 \cdot OMe$.

On crystallising the methylic compound from ethylic alcohol, the *ethylic* compound, $C_6H_2(NO_2)_3 \cdot OEt, EtONa$, is produced; this closely resembles the former but yields ethylic picrate on treatment with acids.

The *propylic* compound, $C_6H_2(NO_2)_3 \cdot OPr, PrONa$, resembles the methylic compound, and is similarly prepared. On treatment with acids, *propylic picrate*, $C_6H_2(NO_2)_3 \cdot OPr$, is obtained, which crystallises in almost colourless needles and melts at 43° .

The *isoamylic* compound, $C_6H_2(NO_2)_3 \cdot OC_5H_{11}, C_5H_{11}ONa$, forms an amorphous, orange precipitate, and when treated with acids yields isoamylic alcohol and *isoamylic picrate*; the latter crystallises in almost colourless, hexagonal plates which melt at $68-69^\circ$. The *benzylic* compound, $C_6H_2(NO_2)_3 \cdot OC_6H_5, C_6H_5ONa$, forms red needles and exhibits fluorescence. *Benzylic picrate*, $C_6H_2(NO_2)_3 \cdot O \cdot CH_2Ph$, is sparingly soluble in alcohol and crystallises in nearly colourless plates which melt at 115° .

When picryl chloride, or trinitranisole, dissolved in methylic alcohol, is treated with an aqueous solution of barium hydroxide, a compound separates in red crystals apparently of the formula



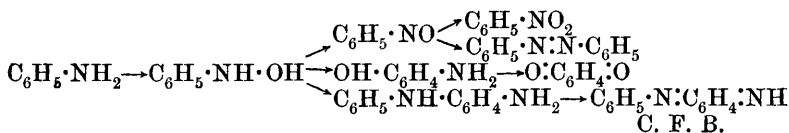
when dried at $110-130^\circ$, it loses water and its composition then approximates to that indicated by the formula $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OMe}]_2, \text{BaH}_2\text{O}_2$. The anhydrous compound is dark crimson, but on exposure to air it absorbs water and regains the scarlet colour of the hydrated substance; acids decompose it, yielding trinitranisole. Calcium hydroxide gives rise to a similar compound, which is more unstable. G. T. M.

Bromoveratrole. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1897, [iii], 17, 114).—The bromoveratrole which Gaspari (*Abstr.*, 1897, i, 30) obtained by the action of bromine on veratrole in acetic acid solution, appears to be identical with the product prepared by the author by diazotising veratrylamine in presence of hydrobromic acid and finely divided copper (*Abstr.*, 1896, i, 426). Both are represented by the formula $\text{C}_6\text{H}_3\text{Br}(\text{OMe})_2$ [$\text{Br} : \text{OMe} : \text{OMe} = 1 : 3 : 4$]. N. L.

Action of Iodine on the Lead Derivative of Catechol. By CHARLES LORING JACKSON and WALDEMAR KOCH (*Ber.*, 1898, 31, 1457—1460).—If quinol is dissolved in water, neutralised with the calculated quantity of potassium hydroxide, and then treated with the calculated quantity of lead acetate, a lead derivative is obtained; when a concentrated alcoholic solution of iodine is added to this, lead iodide is precipitated, and ordinary quinone can be extracted from the aqueous solution.

When the same operations are gone through with catechol instead of quinol, a red chloroform extract is obtained, but no crystalline substance can be isolated from it. This solution contains no catechol; it must be assumed to contain orthobenzoquinone, for when it is shaken with ammonium sulphide solution, sulphur is deposited and catechol is formed; when gaseous hydrogen chloride is passed into it, monochlorocatechol is formed; and when it is boiled with an excess of aniline a dianilidoquinoneanil, $\text{O}:\text{C}_6\text{H}_2(\text{NHPh})_2:\text{NPh}$ [$\text{O}:\text{NPh}:(\text{NHPh})_2 = 1:4:2:5$], melting at 203° , is formed, identical with that obtained from the paraquinone. C. F. B.

The Oxidation of Aniline. By EUGEN BAMBERGER and FRED TSCHIRNER (*Ber.*, 1898, 31, 1522—1528).—When aniline is oxidised with free hypochlorous acid (not bleaching powder), in addition to azobenzene, &c., small quantities of paramidophenol, benzoquinone-chlorimide, $\text{O}:\text{C}_6\text{H}_4:\text{NCl}$, and paramidodiphenylamine are formed. The paramidophenol was undoubtedly formed by the molecular transformation of phenylhydroxylamine, and the paramidodiphenylamine by the action of the last substance on aniline; it was not possible to detect phenylhydroxylamine amongst the products of oxidation of aniline, it is true, but nitrosobenzene, a substance into which it is converted very easily, can be obtained in considerable amount by oxidising aniline in sulphuric acid solution with potassium permanganate, in the presence of a little formaldehyde. The various stages in the oxidation of aniline can now be represented by the following schedule:—



Action of Nitric Acid on Tribromacetanilide. By WILLIAM B. BENTLEY (*Amer. Chem. J.*, 1898, 20, 472—481).—The author has endeavoured to prepare the tribromonitriline melting at 214—215° which Remmers (this Journal, 1874, 696) described as being obtained by acetylating symmetrical tribromaniline, nitrating the anilide, and hydrolysing the resulting nitro-compound with aqueous or alcoholic ammonia in sealed tubes at 180—200°. Körner's preparation obtained from metanitriline melted at 102·5°, and is, therefore, not identical with Remmers'.

The author easily obtained tribromacetanilide, but was unable to prepare tribromonitracetanilide, for fuming nitric acid acted on tribromacetanilide at the ordinary temperature, but only yielded oily products mixed with unaltered anilide. Tetrabromobenzene was the only product which could be recognised when the tribromo-compound was boiled with concentrated nitric acid. On heating the anilide with 80 per cent. acetic acid and nitric acid (sp. gr. 1·4), bromanil, dibromodinitromethane, and oxalic acid were formed. As a means of characterising the bromanil, the author endeavoured to prepare the dibromodiphenoxyquinone described by Jackson and Grindley, but on treating bromanil with sodium phenoxide in absolute alcohol, *dibromodiethoxyquinone* is obtained; it crystallises from alcohol in orange-red prisms, and melts at 139°. Since this substance can also be obtained from bromanil made by Stenhouse's method, there can be no doubt as to the identity of the compound obtained in the author's experiments with the latter. Jackson and Grindley's dibromodiphenoxyquinone is obtained by using 95 per cent. alcohol in the above reaction. G. T. M.

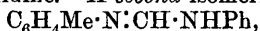
Reactions of Organic Ammonium Salts—Correction. By JULIUS TAFEL (*Ber.*, 1898, 31, 1349).—The benzene ring in phenyltrimethylammonium bromide (this vol., i, 471) is not acted on by chlorine or bromine, but the salt itself, like all quaternary ammonium salts, combines with bromine to form a *perbromide*, $\text{NMe}_3\text{PhBr}_3$, which crystallises from warm alcohol in yellowish-red needles melting at about 112°. When its acetone solution is gently warmed, it yields the colourless phenyltrimethylammonium bromide. J. J. S.

Isomeric Phenyltolylmethenylamidines. By O. ZWINGENBERGER and REINHOLD WALTHER (*J. pr. Chem.*, 1898, [ii], 57, 209—231).—Diphenylmethenylamidine, $\text{NPh}:\text{CH}:\text{NHPh}$, was prepared by adding a mixture of aniline and formanilide to excess of phosphorus trichloride; the product is identical with that prepared from aniline and ethylic orthoformate; the *picrate* and *platinochloride* melt at 187° and 228° respectively. Those of diparatolylmethenylamidine (prepared from paratoluidine and ethylic orthoformate) both melt at 211°.

One *phenylparatolylmethenylamidine*, presumably with the constitution $\text{NPh}:\text{CH}:\text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, is obtained from aniline, formoparatolu-

ide, and phosphorus trichloride; it melts at 98° , its *picrate* and *platinochloride* at 196° and 207° . A *second*, presumably with the same constitution, is obtained by heating diphenylmethenylamidine with paratoluidine at 100° ; it melts at 120° , its *picrate* and *platinochloride* at 178° and 213° . Yet a *third*, presumably with the constitution $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{CH}\cdot\text{NHPh}$, is obtained from paratoluidine, form-anilide, and phosphorus trichloride; it melts at 102° , its *picrate* and *platinochloride* at 193° and 218° . And a *fourth*, presumably with the same constitution as the last, is obtained by heating diparatolylmethenylamidine with aniline hydrochloride in alcoholic solution; it melts at 132° , its *picrate* and *platinochloride* at 209° and 127° . These substances are all different; although the melting point 98° seems near to 102° , the first of the substances in question is twice as soluble in light petroleum as the second. When boiled in light petroleum solution for 5 hours, the compound melting at 98° is converted into that melting at 102° . An attempt to prepare a fifth isomeride, $\text{NPh}\cdot\text{CH}\cdot\text{NMePh}$, failed; no stable product is obtained when diphenylmethenylamidine is heated with methylic (or ethylic) iodide. Neither will this amidine yield an acetic or benzoic derivative; acet-anilide and benzanilide were obtained instead. Cold fuming nitric acid oxidises it to paranitraniline. It will not react with phenylcarbimide; it does, however, react with hydroxylamine hydrochloride and with phenylhydrazine when heated with these substances, the products being *phenylmethenylamidoxime*, $\text{NOH}\cdot\text{CH}\cdot\text{NHPh}$, melting at 128 — 129° , and *diphenylmethenylhydrazidine*, $\text{NHPh}\cdot\text{N}:\text{CH}\cdot\text{NHPh}$, melting at 90 — 91° .

A *phenylorthotolylmethenylamidine*, $\text{NPh}\cdot\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained from formorthotoluidide, aniline, and phosphorus trichloride, and melts at 100° , its *picrate* and *platinochloride* at 168 — 169° and 206 — 207° . An identical substance is obtained, although the yield is not good, by heating aniline with diorthotolylmethenylamidine; the *picrate* and *platinochloride* are also identical with the above. The same substance is yet again obtained by heating diphenylmethenylamidine with orthotoluidine. A *second* isomeride,



is, however, obtained from orthotoluidine, form-anilide, and phosphorus trichloride; it melts at 109 — 110° , its *picrate* and *platinochloride* at 176° and 209 — 210° respectively. The compound melting at 100° can be partially converted into that melting at 110° by boiling it in light petroleum solution; before the conversion is complete, however, decomposition sets in.

The substances described in the paper were crystallised from light petroleum, as a rule. The *picrates* and *platinochlorides* were yellow.

C. F. B.

Reaction of Phenylhydroxylamine with Alcoholic Sulphuric Acid and with Aniline. By EUGEN BAMBERGER and JAN LAGUTT (*Ber.*, 1898, 31, 1500—1508).—The authors, like Haber (*Zeit. Elektrochem.*, No. 22), have also studied the action of alcoholic sulphuric acid on phenylhydroxylamine. When 100 grams of phenylhydroxylamine were digested with 2400 c.c. of commercial absolute alcohol and 50 c.c.

of sulphuric acid (sp. gr. 1·84) for 26 hours on the water bath (in two lots), the weights (in grams) of the following products obtained were:—Azoxybenzene, 14; paraphenetidine, 46; orthophenetidine, 8; paramidophenol, 3·5; orthamidophenol, 3·5; aniline, 4; dark fluorescent oil, 2; nitrobenzene, phenol, and a base resembling a semidine (probably paramidodiphenylamine), traces; colouring matters, not determined. The formation of orthamidophenol (and orthophenetidine) is noteworthy, for, under the influence of aqueous sulphuric acid, only paramidophenol has hitherto been obtained. How the phenetidines are formed is not quite clear; they cannot be formed from the amidophenols, for these give no ethylic derivatives when heated with alcoholic sulphuric acid; nor can they be formed by an intramolecular transformation of the ethylic derivative of phenylhydroxylamine, for this substance does not yield such a derivative when heated with alcoholic sulphuric or hydrochloric acid (neither does *benzyl*hydroxylamine).

When 75 grams of phenylhydroxylamine dissolved in 100 grams of freshly-distilled, dry aniline is added gradually to a mixture of 105 grams aniline hydrochloride with 130 grams aniline already heated to 130°, rinsed in with 15 grams of aniline and the whole then maintained at that temperature for 40 minutes, there are obtained:—Azoxy- (and azo-) benzene, 17—18; colouring matters, 18—19; benzidine sulphate, 10; paramidodiphenylamine sulphate, 8·6; orthamidodiphenylamine and a little diphenylene (?), 6·4; aniline, not estimated; bases of the paramidodiphenylamine type (anilides of amidodiphenylamines?) and chloraniline, traces.

From the final mother liquor, obtained after nitrosophenylhydroxylamine has been allowed to decompose spontaneously in benzene solution, and the products already described (this vol., i, 366) have been separated, a very small quantity of diphenyl can be obtained by evaporating the benzene, and reducing the residue with stannous chloride and boiling hydrochloric acid.

C. F. B.

Reaction of the Nitrosoaliphyls with Concentrated Sulphuric Acid. By EUGEN BAMBERGER, HANS BÜSDORF, and H. SAND (*Ber.*, 1898, 31, 1513—1522).—Nitrosoaliphyls react very readily with concentrated sulphuric acid at 0°, and a yellow product is precipitated on diluting with water; the reaction is of the nature of an aldol condensation; from nitrosobenzene, for example, *nitrosodiphenylhydroxylamine*, $\text{OH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$, is formed. This substance decomposes at 147—152°, and has acid properties; it is reduced by zinc dust and water to paramidodiphenylamine, and by sulphurous acid to a new *paramidodiphenylaminesulphonic acid*, which yields paramidodiphenylamine when it is distilled with ammonium chloride; it forms a dark yellow *monacetyl* derivative, melting between 146° and 157°; when treated with nitric oxide, it yields diazodiphenylamine nitrate, which unites with β -naphthol to form a brownish-black *azo-dye* melting at 164—165° and identical with the product prepared by diazotising paramidodiphenylamine and uniting the product with β -naphthol.

4-Nitroso-2':3-ditolylhydroxylamine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO} + \text{H}_2\text{O}$, from orthonitrosotoluene, decomposes at about 130°; the yellow

monobenzoyl derivative melts and decomposes at 181—182°; when reduced, it yields 4-*amido*-2':3-*ditolylamine*, which melts at 63—64°, is very unstable in the air, and yields a *monacetyl* derivative melting at 122·5°, and a yellow *salicylidene* derivative melting at 112°. 2':3-*Dibromo-4-nitrosodiphenylhydroxylamine*, from *orthobromonitrosobenzene* (which melts at 97·5—98°), melts and decomposes between 118° and 123°, its *monacetyl* derivative at 144—145°; when reduced, it yields 2':3-*dibromo-4-amidodiphenylamine*, which melts at 70°, and froths up when heated in a test-tube, leaving a residue from which alcohol extracts a blue colouring-matter.

When *paranitrosotoluene* is treated with strong sulphuric acid, one bromine atom is lost and 4'-*bromo-4-nitrosodiphenylhydroxylamine* is formed; this decomposes at 154°.

The *salicylidene* derivatives of *amidodiphenylamines* are decomposed by *phenylhydrazines*; with *phenylhydrazine*, *salicylideneparamidodiphenylamine* yields colourless (not yellow) *salicylic phenylhydrazone* and *amidodiphenylamine*; with *paranitrophenylhydrazine*, orange-red *salicylic paranitrophenylhydrazone*, melting at 223°, is formed. From *salicylideneparamidoditolylamine* and *phenylhydrazine*, *salicylic phenylhydrazone* and *paramidoditolylamine* are formed. C. F. B.

The Decomposition of Diazo-compounds. By E. C. FRANKLIN (*Amer. Chem. J.*, 1898, 20, 455—466).—The author gives a detailed account of the method he employs in preparing *ortho*- and *meta*-*amidobenzenesulphonic acids*. The three *amidobenzenesulphonic acids* differ somewhat in their susceptibility to the action of *nitrous acid*. The *ortho*-acid, suspended in a finely divided condition in *ethylic alcohol*, is easily diazotised when subjected to the action of *nitrous fumes*, whilst with the *para*-acid when thus treated the action is never complete, and the *meta*-acid cannot be satisfactorily diazotised in *alcohol*, although when suspended in *water* the reaction proceeds quite readily.

The decomposition of the *para*- and *meta*-*diazobenzenesulphonic acids* by *methylic* and *ethylic alcohols* has been previously studied by Shober and Kiefer (*Abstr.*, 1893, i, 639; and 1895, i, 520), and the author now furnishes the results obtained in the case of the third isomeride.

Orthodiazobenzenesulphonic acid, when decomposed by *methylic alcohol*, yields only *orthomethoxybenzenesulphonic acid*, which is identified by means of its *chloride* and *amide*; the *methoxy-compound* is the sole product whether the action be carried out under *atmospheric pressure* or under greater or less pressures. Similarly, *orthoethoxybenzenesulphonic acid* is the only product of the action of *ethylic alcohol*. This behaviour of the *ortho*-acid is contrasted with that of its two isomerides; thus in the case of the *meta*-compound substitution of *hydrogen* occurs, especially at the lower pressures and when the higher *alcohol* is employed, whilst the *para*-compound yields chiefly *benzenesulphonic acid*, except when *methylic alcohol* acts on it under increased pressure; in this case, *methoxybenzenesulphonic acid* predominates.

When *paramethoxybenzenesulphonamide* is added to well-cooled

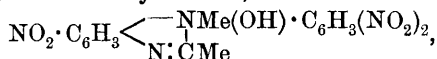
fuming nitric acid and the liquid is diluted with water, a small quantity of metadinitrobenzene is obtained; the filtrate after removing the nitric acid by evaporation with alcohol and neutralising with potash, yields the *potassium* salt of a mononitroparamethoxybenzenesulphonic acid; its *sulphonamide* forms yellow needles and melts at 138—140°.

A considerable amount of metadinitrobenzene is obtained on nitrating paraethoxybenzenesulphonamide. Orthomethoxybenzenesulphonamide, on nitration, yields a small quantity of metadinitrobenzene, but this compound is not obtained on nitrating the metasulphonamide.
G. T. M.

Azammonium Compounds. By RUDOLF NIETZKI and ALFRED RAILLARD (*Ber.*, 1898, 31, 1460—1464).—When dinitrodiphenylmethylamine, $\text{NMePh} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ [$\text{N} : (\text{NO}_2)_2 = 1 : 2 : 4$] (Leymann, *Abstr.*, 1882, 1057), is dissolved in acetic acid, treated with fuming nitric acid, and allowed to remain, *tetranitrodiphenylmethylamine*, presumably $\text{NMe}[\text{C}_6\text{H}_3(\text{NO}_2)_2]_2$ [$\text{NMe} : (\text{NO}_2)_2 = 1 : 2 : 4 = 1' : 2' : 4'$], is formed; this is yellow and melts at 210°.

When it is suspended in aqueous-alcoholic ammonia, and hydrogen sulphide is passed in, no considerable rise of temperature being allowed to take place, *amidodinitrodiphenylmethylamine*,

$\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{NMe} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ [$\text{NH}_2 = 2$], melting at 190°, is formed. When this is boiled with excess of acetic anhydride, it yields an anhydro-base,

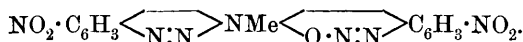


which is yellow, and melts at 264°.

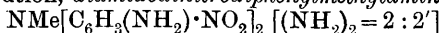
When treated with nitrous acid, it yields trinitrodiphenylmethylazammonium hydroxide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \overline{\text{NMe}(\text{OH}) \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2}$; this is

yellow, has no determinate melting point, and no basic properties; it can be reduced by ammonium sulphide to an orange-red *amido*-compound, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \overline{\text{NMe}(\text{OH})} > \text{C}_6\text{H}_3 \cdot \text{NO}_2$ [$\text{NH}_2 = 2'$], and when this

is treated with nitrous acid a yellow product is obtained which does not melt without decomposing, and probably has the constitution



If, in the reduction of tetranitrodiphenylmethylamine with ammonium sulphide, the temperature is allowed to rise to the boiling point of the solution, *diamidodinitrodiphenylmethylamine*,



is formed; nitrous acid converts it into the substance mentioned at the end of the last paragraph.
C. F. B.

Ketone Musks. By ALBERT BAUR-THURGAU (*Ber.*, 1898, 31, 1344—1349).—When the ketone obtained by introducing a benzoyl group into butyltoluene is nitrated, no compound of musk-like odour is obtained; if, however, an acetyl group is introduced into butyltoluene

or butylxylene and the methyl ketones thus obtained are nitrated, products are obtained which have a strong odour of musk.

Butyltoluene (1 part), carbon bisulphide (10 parts) and aluminium chloride (6 parts) are cooled in a flask, and acetic chloride (6 parts) run in as quickly as possible; after distillation on the water bath, the residue is poured on to ice and treated in the usual manner. The *acetyl* derivative is obtained as an oil with a pleasant aromatic odour boiling at 255—258°. When nitrated at 0° with 100 per cent. nitric acid, a *dinitro*-derivative, $C_{13}H_{16}N_2O_5$, is obtained; it crystallises in broad needles, melts at 131°, and has a strong odour of musk. The acetyl group in this compound does not occupy the symmetrical position, but takes the place of one of the nitro-groups in butyltrinitrotoluene. When 1 : 3 : 5-butylxylene is oxidised by boiling for 3 days with dilute nitric acid, *butyltoluic acid* is obtained; this is readily soluble in dilute alcohol, sparingly in light petroleum, and crystallises in colourless plates melting at 162°. The *acid chloride* is a liquid boiling at 258—260°, and when treated with sodium ethylic acetoacetate, and the product thus obtained hydrolysed, a solid *ketone*, $C_{13}H_{18}O$, melting at 47° and boiling at 260°, is obtained; it yields a *dinitro*-derivative melting at 103° which has no musk-like odour.

Butylxyl methyl ketone, $C_{14}H_{20}O$, obtained by slowly adding acetic chloride (50 grams) to butylxylene (100 grams) and aluminium chloride (30 grams) and treating in the usual manner, crystallises from ether in large plates melting at 48° and boiling at 265°, and is readily soluble in alcohol, benzene, and light petroleum. It does not react with hydroxylamine, nor yet with phenylhydrazine, and when treated at 0° with 100 per cent. nitric acid yields a *dinitro*-derivative, $C_{14}H_{18}N_2O_5$, melting at 136° and having an odour of musk. This nitro-derivative does not yield an oxime or a phenylhydrazone, but yields a *benzylidene* derivative melting at 140° and a *trichlorethylidene* derivative melting at 179°.

When oxidised with alkaline permanganate below 65°, butylxyl methyl ketone yields *butylxylglyoxylic acid*, which cannot be crystallised and which melts, by no means sharply, at 90—110°. Its *methyl* salt is an oil, but yields a *dinitro*-derivative, $C_{15}H_{18}N_2O_7$, melting at 127°. The glyoxylic acid, when heated with Nordhausen sulphuric acid, yields *butylxylcarboxylic acid* melting at 168°, and readily soluble in alcohol or benzene, but when heated with aniline or paratoluidine according to Bouveault's method, *butylxylaldehyde* is obtained. When reduced, the glyoxylic acid is converted into *dimethylbutylmandelic acid*, $C_4H_9 \cdot C_6H_5 \cdot Me_2 \cdot CH(OH) \cdot COOH$, which crystallises in colourless plates melting at 120°. When the ketone is oxidised with alkaline permanganate at temperatures above 70°, the products are butylxylcarboxylic acid, the glyoxyl-carboxylic acid, and the dicarboxylic acid. The filtrate from the manganese dioxide is acidified, and the oily mixture of acids is added in small portions at a time to boiling 40—50 per cent. sulphuric acid to which an equal weight of zinc dust is slowly added. When cold, the mixture is filtered and the residue extracted with sodium carbonate, and the acid obtained by acidifying the alkaline solution is heated in an oil bath to 200°; the fused mass then consists of butylxylcarboxylic acid, *butylmethylphthalide* and *butyl*-

phthalidecarboxylic acid; the phthalide, which remains behind when the mixture is extracted with sodium carbonate solution, has a slight smell of benzaldehyde, is readily soluble in the usual solvents with the exception of water, and when nitrated with 100 per cent. nitric acid yields two isomeric *mononitro*-derivatives; the one melts at 154° and is readily soluble in alcohol, and the other melts at 181° and is more sparingly soluble. Butylxylylcarboxylic acid (m. p. 168°) is obtained from the mixture of the two acids by extraction with 50 per cent. alcohol; the phthalidecarboxylic acid crystallises from absolute alcohol in colourless needles melting at 273° .

When the ketone is oxidised with dilute nitric acid, the chief product is Hollemann's dinitrosacyl (Abstr., 1888, 275), which, when warmed with sodium hydroxide solution, yields butylxylylcarboxylic acid. When the oxidising agent employed is 60 per cent. nitric acid, the product is *dinitrodinitrosacyl*, $(C_{14}H_{16}N_2O_4)_2$, which crystallises from alcohol in needles melting at 176° , and when warmed with sodium hydroxide yields *nitrobutylxylylcarboxylic acid*, melting at 190° . *Tetranitrodinitrosacyl*, formed when 100 per cent. nitric acid is used, crystallises from chloroform in thick prisms, melts at 245° , and is insoluble in alcohol or light petroleum; when warmed with alkali, it yields *dinitrobutylxylylcarboxylic acid* melting at 236° . The *methylic* salt of this acid is obtained when the *acid chloride*, which crystallises from benzene in needles melting at 99° , is treated with sodium methoxide; it crystallises from alcohol in pale yellow needles melting at 96° .

When ketone musk is oxidised with potassium permanganate under exactly the same conditions as were employed for the ketone, the product is a dinitroglyoxylic acid, which could not be obtained in a crystalline form, and the methylic salt of which has been previously described. When oxidised in acetic acid solution with either permanganate or chromic anhydride, the product is the dinitro-acid melting at 236° .

Butylxylyl butyl ketone, $C_{16}H_{24}O$, melts at 50° and distils at $290-295^{\circ}$ its *dinitro*-derivative melts at 128° and smells like musk. *Butylxylyl amyl ketone* is an aromatic oil distilling at $185-190^{\circ}$ under 14 mm. pressure; its *dinitro*-derivative crystallises from alcohol in long, yellow needles melting at 151° , and has a strong odour of musk. J. J. S.

Nitration of Methylic Benzoate. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1898, 17, 96-99).—On nitration, methylic benzoate gives rise to products similar to those obtained from benzoic acid; the methyl group is therefore without influence. Methylic metanitrobenzoate is the principal product of the action at 0° ; a small proportion, however, of *methylic orthonitrobenzoate* is formed; this is a slightly yellow liquid which boils at 183° under a pressure of 22 mm., has a sp. gr. = 1.2855 at 20° , and, when solidified, melts at -13° . It is best prepared by adding silver benzoate to well-cooled methylic iodide; it is also formed on passing hydrogen chloride into a solution of benzoic acid in methylic alcohol, or by heating the latter solution with sulphuric acid; in both cases, however, the yield is poor.

W. A. D.

Separation of Ortho- and Meta-nitrobenzoic Acids. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1898, 17, 100--101).—When hydrogen chloride is passed through a solution of ortho- and meta-nitrobenzoic acids in methylic alcohol, the meta-acid is converted completely into its methylic salt, whilst only a small proportion of the ortho-salt is produced; crystals of methylic metanitrobenzoate separate on cooling, whilst the ortho-salt, being a liquid, remains dissolved. After purification, the meta-methylic salt is easily hydrolysed by baryta water.

W. A. D.

Some Properties of Aromatic Orthohydroxy-compounds. By ISIDOR TRAUBE (*Ber.*, 1898, 31, 1566—1571).—The molecular volume in solution of sodium salicylate is different from that of sodium para- or meta-hydroxybenzoate, and agrees well with that calculated on the assumption that the acid has some such constitution as $\text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{COOH}$; no such difference is to be observed

between sodium ortho- and meta-hydroxyhexahydrobenzoates. In accordance with this view is the fact that salicylic acid, unlike its two isomerides, develops practically no heat when mixed with a second molecule of soda; other physical properties also afford confirmatory evidence. Further, salicylic acid in different solvents gives, with ferric chloride, a series of colours very similar to those given by ethylic acetoacetate (probably it is not hydroxy-compounds that alone give colorations with ferric chloride, but mainly aromatic keto-compounds that give red or violet colorations; compare Morrell and Crofts, *Trans.*, 1898, 345). Salicylic acid would appear not to be a mixture of two isomerides, for the specific gravity of an alcoholic solution of ethylic salicylate does not alter with the time.

Again, catechol has a smaller volume in solution than resorcinol or quinol, and, unlike the last two, it gives out little heat when mixed with a second molecule of soda. Probably it is a mixture of two isomerides, *k* and *e*, which give respectively a deep red and a green coloration with ferric chloride.

C. F. B.

Phenylglutaric Acid and its Derivatives. By SAMUEL AVERY and ROSA BOUTON (*Amer. Chém. J.*, 1898, 20, 509—515).—The authors find that benzylidene chloride and ethylic sodiomalonate do not give rise to ethylic benzylidenedimalonate, but to ethylic benzylidene malonate. The latter substance, when treated with ethylic sodiomalonate in alcoholic solution, and subsequently acidified with dilute sulphuric acid, yields an oil which appears to consist chiefly of ethylic benzylidenedimalonate. On boiling this oil with strong hydrobromic acid for 24 hours, evaporating the product to dryness, extracting the residue with hot water, and crystallising from dilute hydrochloric acid, β -phenylglutaric acid is obtained; it forms glistening plates soluble in water, alcohol, ether and chloroform, and benzene, insoluble in light petroleum, and melts at 140°. It is identical with the acid obtained by Michael by the action of ethylic sodiomalonate on an alkylcinnamate. The barium, copper, lead, and alkali salts are described.

β -Phenylglutaric anhydride, produced when the acid is heated above its melting point, or when treated with acetic chloride, forms glisten-

ing, white plates and melts at 105° ; it is soluble in benzene, chloroform, and ether, insoluble in light petroleum. *β -Phenylglutaranilic acid*, formed from aniline and the anhydride, melts at 168° . *β -Phenylglutaranil*, obtained on heating the preceding compound, forms glistening, white needles melting at 223° . *β -Phenylglutaroparatolilic acid* melts at 154 — 155° .

When fuming sulphuric acid acts on β -phenylglutaric anhydride, a crystalline acid melting at 153° is produced; its silver salt has the composition $C_{22}H_{18}O_6Ag_2$. G. T. M.

β -Phenyl- α -methylglutaric Acid. By SAMUEL AVERY and MARY L. FOSSLER (*Amer. Chem. J.*, 1898, 20, 516—518).—The product of the condensation of ethylic sodiomalonate with methylic α -methylcinnamate when hydrolysed, and subsequently distilled, yields an oil which is probably the impure anhydride of the above acid. The copper salt, formed on adding copper sulphate to the anhydride dissolved in ammonia, is decomposed by hydrogen sulphide, and the free β -phenyl- α -methylglutaric acid is obtained on concentrating the solution. It forms flaky, white plates, melts at 122° , and is soluble in alcohol, ether, chloroform, and hot benzene, insoluble in light petroleum. G. T. M.

Action of Phthalic Anhydride on Para- and on Meta-hydroxydiphenylamine. By ARNALDO PIUTTI and R. PICCOLI (*Ber.*, 1898, 31, 1327—1333. Compare *Abstr.*, 1884, 448).—When molecular quantities of phthalic anhydride and parahydroxydiphenylamine are heated together on a sand-bath, the mixture begins to melt at 60° , water is given off at 150° , and the mass solidifies and melts again at 150 — 195° ; after keeping at this temperature for some time, the mass is pounded and extracted with sodium carbonate solution, and this extract, when acidified, yields *parahydroxydiphenylphthalamic acid*, $OH \cdot C_6H_4 \cdot NPh \cdot CO \cdot C_6H_4 \cdot COOH$. It crystallises from dilute alcohol in somewhat yellowish prisms melting at 191 — 192° , and is insoluble in water, but readily dissolves in alcohol, ether, or acetic acid. With concentrated sulphuric acid, it yields a blue coloration, which disappears on the addition of alcohol or water. When heated above its melting point, the acid yields an *anhydride*. The silver salt, $C_{20}H_{14}NO_4Ag + 3\frac{1}{2}H_2O$, and copper salt, $(C_{20}H_{14}NO_4)_2Cu + 4H_2O$, are both described. The *ethylic* salt crystallises in needles melting at 166 — 168° . *Paramethoxydiphenylphthalamic acid*, obtained by treating an alcoholic solution of the hydroxy-acid with potassium hydroxide and methylic iodide, can best be purified by dissolution in alcohol and fractional precipitation with water; it is insoluble in water, but dissolves readily in alcohol, ether, or acetone, and melts at 90 — 92° ; the corresponding *ethoxy*-derivative melts at 80 — 82° . Sparingly soluble *acetyl* and *benzoyl* derivatives have been obtained, and they, together with the above-mentioned compounds, yield the characteristic coloration with sulphuric acid.

The residue left after extraction with sodium carbonate consists of a coloured substance which is insoluble in the usual solvents but dissolves in sulphuric acid; the addition of water to this solution precipitates a strongly coloured resin. The same coloured product is

obtained when an excess of parahydroxydiphenylamine reacts with phthalic anhydride.

Molecular quantities of the anhydride and metahydroxydiphenylamine react in pretty much the same manner; the mixture is completely fused at 120° , and at a higher temperature becomes solid again; when purified by crystallisation from alcohol, *metahydroxydiphenylphthalamic acid* is obtained in the form of yellowish crusts, which turn violet at 185° and melt at 191 — 192° ; the *sodium*, *potassium*, *ammonium*, and *silver* salts have been prepared. When heated at its melting point, the acid loses water, and is converted into the corresponding rhodamine; dehydrating agents yield the same product. The *ethylic* salt melts at 155 — 157° , the *methoxy*-derivative melts at 95 — 98° and becomes coloured at 120° , and the *ethoxy*-derivative melts at 90° .

The *rhodamine*, $C_{32}H_{22}N_2O_3$, is obtained when phthalic anhydride (1 mol.) is heated with metahydroxydiphenylamine (2 mols.) at about 150 — 160° for 2 hours, and can best be purified by repeated extraction with alcohol; it is sparingly soluble in ether, more readily in benzene or carbon bisulphide, yielding colourless solutions. Its *hydrochloride* forms small, violet crystals, and when its alcoholic solution is treated with bromine, the violet colour is partially destroyed.

In a single instance the mother liquors from the rhodamine yielded a crystalline compound melting at 207° , and possessing the properties of phenylphthalimide.

J. J. S.

Action of Ethylic Oxalate on Paramidophenol and its Ethers. By ARNALDO PIUTTI and R. PICCOLI (*Arch. Pharm.*, 1898, 236, 153—160, and *Gazzetta*, 28, i, 284—298).—See this vol., i, 319.

E. W. W.

Aromatic Sulphamic Acids—Correction. By CARL PAAL (*Ber.*, 1898, 31, 1327). In reply to Junghahn (this vol., i, 479), the author states that free sulphamic acids, namely, paratolyl- and α -naphthyl-sulphamic acids, were prepared some two years ago by Jänicke Lowitsch and himself (*Abstr.*, 1896, i, 235; 1897, i, 351).

J. J. S.

Action of Oxides of Nitrogen on Mercury Alkyls. By JAKOB KUNZ (*Ber.*, 1898, 31, 1528—1531. Compare Bamberger, *Abstr.*, 1897, i, 288).—When mercury paratolyl, $(C_6H_4Me)_2Hg$, is mixed with nitrogen trioxide at 0 — 15° , the product is mercuryparatolyl nitrate, $C_6H_4Me \cdot Hg \cdot NO_3$, together with paratolyldiazonium nitrate and a little paranitrosotoluene. With nitrogen tetroxide under similar circumstances, it gives mercuryparatolyl nitrate and paranitrosobenzene. With nitric oxide, no reaction takes place in the absence of air; when air is admitted, the same products are obtained as with nitrogen trioxide. Mercuryorthoditolyl behaves in the same way as the para-compound.

Mercury- α -dinaphthyl yields, with nitrogen trioxide, mercury- α -naphthyl nitrate and α -naphthyldiazonium nitrate, but no nitroso-naphthalene. With nitrogen tetroxide, it yields mercury- α -naphthyl nitrate and some naphthalene, but neither α -naphthyldiazonium nitrate nor nitrosonaphthalene.

C. F. B.

Tetrahydropyrene Compounds. By PAVEL IW. PETRENKO-KRITSCHENKO (*Ber.*, 1898, 31, 1508—1512).—When a mixture of acetonedicarboxylic acid (1 mol.) and methylsalicylaldehyde (2 mols.) with an equal volume of acetic acid and some hydrochloric acid is allowed to remain overnight, *dimethoxydiphenyltetrahydropyrenedicarboxylic acid*, $\text{CO} \begin{array}{c} \text{CH}(\text{COOH}) \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \\ \text{CH}(\text{COOH}) \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{array} \text{O}$, is formed. When heated on the water bath, this loses carbonic anhydride and yields *dimethoxydiphenyltetrahydropyrene*, $\text{CO} \begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \\ \text{CH}_2 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{array} \text{O}$, which melts at 173°. Boiling with acetic anhydride does not convert this into an unsaturated ketone, but heating it in alcoholic solution with a few drops of hydrochloric acid for $\frac{1}{4}$ hour on the water bath does effect this conversion: *dimethoxydibenzylideneacetone*, $\text{CO}(\text{CH}:\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe})_2$, is yellow and melts at 123°; its *tetrabromide* is colourless and melts at 174°.

When the substituting group in the phenyl residues is not neutral in character, like methoxyl, but acid, no condensation to a pyrene takes place. Acetonedicarboxylic acid and paranitrobenzaldehyde yield an *acid*, $\text{CO}[\text{CH}(\text{COOH}) \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2]_2$, which loses carbonic anhydride when heated on the water bath, forming yellow *diparanitrobenzylideneacetone*, $\text{CO}(\text{CH}:\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$; this melts at 254°, its colourless *tetrabromide* at 239°; it may also be obtained by adding a few drops of aqueous soda to a mixture of paranitrobenzaldehyde with acetone.

Metanitrobenzaldehyde and metachlorobenzaldehyde condense with acetonedicarboxylic acid forming *ketones*, which melt at 239° and 123° respectively.

C. F. B.

Reaction of Benzaldehyde with Phenol. By ARTHUR MICHAEL (*J. pr. Chem.*, 1898, [ii], 334—336).—Benzaldehyde may condense with phenol to dihydroxytriphenylmethane in the presence of a moderate quantity of a mineral acid (Rusanoff, *Abstr.*, 1889, 188), but in the presence of traces only of acid the product is hydroxybenzhydrol, as the author showed previously, for when it is distilled with zinc dust and the distillate is fractionated under diminished pressure diphenylmethane is obtained. The first stage in the interaction between an aldehyde and a phenol undoubtedly consists in an aldol condensation; whether a further condensation takes place between this first product and a second molecule of the phenol depends on the nature of the latter and on the amount of mineral acid present.

C. F. B.

Cedirets. By RUDOLF NIETZKI and R. BERNARD (*Ber.*, 1898, 31, 1334—1338. Compare Nietzki, *Abstr.*, 1878, 868).—The ditolylcediret, $(\text{C}_7\text{H}_5\text{OMe})_2\text{O}_2$, previously obtained by the oxidation of toluquinol methylic ether, when heated with an alcoholic solution of hydroxylamine hydrochloride, yields a *monoxime*, $\text{C}_{16}\text{H}_{17}\text{NO}_4$, crystallising in bronzy, glistening needles, and only sparingly soluble in the usual solvents; it dissolves in alkalis, may be recrystallised from amyl alcohol, and yields a *monacetyl* derivative. When this oxime

is warmed with about six times its weight of nitric acid (sp. gr. 1.3) and the solution allowed to cool, a *nitro*-derivative, $C_{14}H_{11}NO_5$, is obtained, which crystallises from alcohol in beautiful, red needles; when heated with acetic anhydride, the nitro-compound yields an *acetyl* derivative, crystallising in pale yellow needles and melting at 143° . Brunner's ditolyldiquinone (Abstr., 1889, 996) may be obtained by oxidising ditolylcedrret with dilute nitric acid, or by the oxidation of dimethyltoluquinol with chromic acid mixture. The following constitutions agree best with the reactions and methods of preparation of the different compounds.

Nitro-derivative, $NO_2 \cdot C_6H_2Me(OH) \cdot C_6H_2MeO_2$, $NO_2 : Me : OH = 2 : 3 : 5$ and $Me : O_2 = 3' : 2' : 5'$; monoxime,

$C_6H_2Me(OMe)_2 \cdot C_6H_2MeO : NOH$, $Me : (OMe)_2 = 3 : 2 : 5$
and $O : Me : NOH = 2' : 3' : 5'$; ditolylcedrret,

$C_6H_2(OMe)_3 \cdot C_6H_2MeO_2$, $(OMe)_3 = 2 : 3 : 5$
and $O : Me : O = 2' : 3' : 5'$.

J. J. S.

Nitrogen Compounds of the Menthol Series and their Derivatives. By MICHAËL KONOWALOFF and W. TSCHESKY (*Ber.*, 1898, 31, 1478—1481).—When menthone is nitrated with nitric acid of sp. gr. 1.075, in an open vessel, at 80° , with constant stirring, a nitromenthone, probably $C_8H_7 \cdot C(NO_2) < \begin{smallmatrix} CO-CH_2 \\ CH_2-CH_2 \end{smallmatrix} > CHMe$, is formed (Abstr., 1896, i, 177); it has a rotation greater than $+39^\circ$, although the menthone employed was *laevorotatory*. The crude nitromenthone was reduced with tin and hydrochloric acid to *amidomenthone*, $NH_2 \cdot C_{10}H_{17}O$, which boils at about 125° under 25 mm., at $235-237^\circ$ under ordinary pressure, has sp. gr. = 0.9750 at $0^\circ/0^\circ$, 0.9606 at $20^\circ/0^\circ$, and index of refraction $n_D = 1.47397$ at 20° , and is fairly soluble in water. The *hydrochloride* melts and decomposes at $245-247^\circ$; no other salts could be made to crystallise. Amidomenthone forms an *oxime* which boils at $182-185^\circ$ under 20 mm. pressure, the *hydrochloride* of which melts at 110° ; also a *semicarbazone* melting at 80° , and a crystalline *benzoyl* derivative. Amidomenthone in alcoholic solution is reduced by sodium to *mentholamine* (*amidomenthole*), $NH_2 \cdot C_{10}H_{17} \cdot OH$, a viscous liquid boiling at $147-150^\circ$ under 20 mm., and at 254° under ordinary pressure; its specific rotation $[\alpha]_D = -6^\circ$; it is fairly soluble in water. Its *sulphate* melts at 250° ; no other salt could be prepared.

Amidomenthonoxime in alcoholic solution is reduced by sodium to a *diamine*, $C_{10}H_{18}(NH_2)_2$, which boils at $240-243^\circ$; the salts crystallise badly, but the platinochloride and the mercuriochloride were obtained crystallised; the hydrochloride reacts vigorously with potassium nitrite, yielding a liquid which boils at 220° , and is apparently an unsaturated ketone, identical or isomeric with pulegone. C. F. B.

Guaiacum Resin. II. By JOSEF HERZIG and F. SCHIFF (*Monatsh.*, 1898, 19, 95—105. Compare Abstr., 1897, i, 165, 254, and this vol., i, 327).—Pyroguaiacin crystallises from alcohol in beautiful, glistening leaflets melting at $180-183^\circ$, and on analysis gives numbers agreeing with the formula $C_{13}H_{14}O_2$. When treated with acetic anhydride and sodium acetate, it yields *acetylpyroguaiacin*, $OAc \cdot C_{13}H_{13}O$, crystallising

from alcohol in flat, glistening needles melting at 122—124° (compare Weiser, *Monatsh.*, 1880, 1, 594).

Attempts to arrive at the nature of guaiaretic acid have so far proved fruitless, for when the acetyl derivative is oxidised with chromic acid in acetic acid solution no crystalline substance could be obtained. The acid gives a *diethyl* derivative crystallising from alcohol in flat, white needles or leaflets, melting at 100—102° and distilling in a vacuum without decomposition. A. W. C.

Lichens and their Characteristic Constituents. By OSWALD HESSE (*J. pr. Chem.*, 1898, [ii], 57, 232—318. Compare Abstr., 1895, 298).—This long paper contains an account of the constituents of a number of lichens, these constituents being described under the heading of the lichens from which they were obtained respectively. The methods by which they were obtained are described in detail, but it may be said that the method generally adopted was to extract a portion of the lichen, usually in coarse fragments, with 100—200 c.c. of ether in a reflux apparatus until nothing more was dissolved; the ether was as free from alcohol as possible, in some cases entirely so. If no appreciable deposit had formed during 10 hours in the ethereal extract, the latter was used for the extraction of a fresh portion of the lichen. Had a deposit formed, it was filtered off, and the ethereal solution concentrated so as to obtain a fresh quantity of the deposit. Often the ethereal solution was shaken with aqueous potassium hydrogen carbonate; this removed acids (except usnic acid), which were afterwards set free with hydrochloric acid and extracted with ether. Sometimes the filtered ethereal extract was evaporated to dryness; if small quantities of usnic acid were present, this acid was dissolved out by boiling with a mixture of 9 parts of light petroleum and 1 of benzene; or in other cases, the solid residue was treated with a limited quantity of alcohol, the hot solution being filtered from the undissolved part and diluted with water until a turbidity just appeared; or some other of the recognised methods of organic chemistry was employed. Below is a list of the lichens examined, with the localities in which they were found, and the substances obtained from them; where melting points and formulæ differ from those previously assigned by the author or others, the present ones may be assumed to be more correct, the material employed having been purer.

Usnea longissima Acharius, from Garmisch (near Stuttgart?) and Rahmünzsch in the Black Forest.—Usnic acid; the conversion of this substance into decarbusnein is effected particularly easily by heating it with four times its weight of acetone for 4 hours at 150°. [This acid is identical with the old α -usnic acid; the prefix is no longer necessary, as " β -usnic acid" has been shown to be a mixture of usnic acid itself with atranorin]. *Barbatic acid*, $C_{22}H_{24}O_8$ (Stenhouse and Groves, $C_{19}H_{20}O_7$), is monobasic; the *potassium* and *barium* salts, with $1\frac{1}{2}$ and $3H_2O$ respectively, and the green *copper* salt were prepared and analysed. The *ethylic* salt, obtained by heating the potassium salt with ethylic iodide at 150°, melts at 132°; in alcoholic solution, it gives a bluish-violet coloration with ferric chloride.

U. barbata (L.) Fries, from Traunstein, Bavaria.—Usnic and barbatic acids.

U. barbata f. *dasypoga* (Ach.) Fr. and f. *hirta* (L.) Fr., from Java cinchona bark.—Usnic acid. *Usnaric acid*, $C_{30}H_{22}O_{15}$, is but little soluble in ether, except when just liberated from a salt; it crystallises in aggregates of needles, decomposes at $240-260^\circ$ without melting, has a very bitter taste, and gives a purplish-violet to brownish-red coloration with ferric chloride; it is possibly identical with Zopf's salaz(in)ic acid (this vol., i, 90). *Usnarin* crystallises in prisms and melts and decomposes at 180° ; it is insoluble in cold alkalis, and has no taste.

U. ceratina (Ach.).—Usnic acid, barbatic acid, and barbatin.

Evernia vulpina (Ach.), from the Engadine, and also from California, where it occurs on the *Wellingtonia*, and is known as "moss of the big trees."—Vulpic acid and atranorin.

E. divaricata (L.) Ach., from Schörzingen (?).—*Divaricatic acid*, $C_{21}H_{23}O_6 \cdot OMe$, is crystalline, melts at 129° , and gives a purplish-violet coloration with ferric chloride in alcoholic solution; a *barium salt*, $C_{22}H_{24}O_7Ba + 2H_2O$, was prepared and analysed, and in the mother liquor from it another salt, probably of an acid $C_{11}H_{14}O_4$, was found.

E. prunastri (L.) Ach.; var. *vulgaris*, Körber, from near Stuttgart, and var. *gracilis* from Liebenzell, Black Forest.—Evernic acid, usnic acid, and atranorin.

E. furfuracea (L.) Ach., from Feuerbach, near Stuttgart.—Atranorin only.

Ramalina pollinaria (Westr.) Ach., from Feuerbach.—Usnic acid. Atranorin. Evernic acid, $C_{16}H_{13}O_6 \cdot OMe$: the *potassium salt*, $C_{17}H_{15}O_7K + 2H_2O$, was prepared; when this is heated with ethylic iodide and alcohol, it does not form an ethylic salt, but yields ethylic everninate, orcinol, and carbonic anhydride, according to the equation $C_{17}H_{15}O_7K + EtI + H_2O = C_6H_9O_3 \cdot OEt + C_7H_9O_2 + CO_2 + KI$; the acid forms insoluble basic barium and calcium salts; it is decomposed by boiling with baryta water into orcinol and *barium everninate*, $C_9H_8O_4Ba + H_2O$ or $(C_9H_9O_4)_2Ba + 8H_2O$, as the case may be; orcinol is also obtained when the acid is heated with hydriodic acid. Ramalic acid, $C_{16}H_{13}O_6 \cdot OMe$: the anhydrous *potassium* and sparingly soluble *barium* salts were prepared; the acid gives a purplish-violet coloration with ferric chloride; boiled with baryta, it yields the same products as evernic acid does, and no doubt the isomerism between these two acids consists in the different way in which the lactone-condensation has taken place.

Ramalina ceruchis (Ach.), from a specimen of Californian "orseille."—Usnic acid. An acid melting at 135° , fairly soluble in cold alcohol; and another, less soluble, decomposing at $220-260^\circ$ (usnaric acid?).

Rocella Montagnei Bél., from Ceylon, Zanzibar, Madagascar, and Angola.—Erythrin: probably

$C_4H_6(OH)_3 \cdot O \cdot CO \cdot C_6H_2Me(OH) \cdot O \cdot CO \cdot C_6H_2Me(OH)_2$, a condensation product of erythritol with lecanoric acid; crystallises from dilute acetic acid with $1H_2O$ and melts when anhydrous at 148° (not 137°). *Oxyroccellic acid*, $C_{15}H_{30}O(COOH)_2$: melts at 128° ; gives

no coloration with ferric chloride or bleaching-powder solution; the anhydrous *barium* and *silver* salts were prepared and analysed; when heated at 160–180°, the acid yields the *anhydride* which melts at 82°; when heated with acetic anhydride at 85°, it yields an *anhydride*, $O(CO \cdot C_{15}H_{30}O \cdot COOH)_2$, which melts at 121°.

R. fuciformis (L.) D.C.—Erythrin and oxyroccellic acid.

R. peruensis Krempelhuber [syn. *R. cacticola*, Darbshire, and *R. fruticosa* (*fructetosa*) Laurer], from California.—Erythrin. Oxyroccellic acid. Roccellic acid, $C_{17}H_{32}O_4$, a dibasic acid; the *barium*, with $1\frac{1}{2}H_2O$, *calcium*, *copper*, and *silver* hydrogen-salts and the normal *lead* salt were prepared and analysed.

R. tinctoria (L.) Ach., from Cape Verde.—Oxyroccellic, roccellic and parellic acids. Lecanoric acid, $C_{16}H_{14}O_7 + H_2O$, a monobasic acid; gives in alcoholic solution, like erythrin, a blood-red coloration with bleaching-powder solution; the *potassium*, *barium*, *calcium*, *copper*, and *basic lead* salts, with 1, 5, 4, 2 and 0 H_2O respectively, were prepared and analysed; when heated with acetic acid, the acid first yields orsellinic acid, but this readily loses carbonic anhydride, forming orcinol; heated with methylic alcohol at 85°, it yields carbonic anhydride, orcinol, and methylic orsellinate, which melts at 138°, and has a great resemblance to methylic betorcinolcarboxylate. Orsellinic acid crystallises from dilute acetic acid with $1H_2O$, from alcohol with 2 (and 1) H_2O .

R. portentosa Mtg., from Chili.—Lecanoric acid only.

R. canariensis Darbshire, from Teneriffe.—Lecanoric acid only.

R. sinensis Nylander, from Tonquin.—Lecanoric acid.

R. decipiens Darbshire. An acid, sparingly soluble in ether, melting at 142°, and giving a brownish coloration with ferric chloride.

R. intricata (Mtg.) Darbshire. Zeorin. *Roccellaric acid*; crystalline, melts at 110°, gives a bluish-violet coloration with ferric chloride, but none with bleaching-powder solution.

Reinkella birellina Darbshire, from Lima, Peru. Roccellic or oxyroccellic acid. Roccellinin.

Darbshirella gracillima (Krph.) Zahlbruckner (syn. *Roccella intricata* Mtg.), from Chili.—Parellic acid.

Dendrographa leucophæa (Tuck.) Darbshire, from San Diego, Mexico. Protocetraric acid. Further, a crystalline substance which melts at 121°, and gives a brownish-red coloration with ferric chloride.

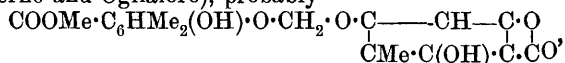
Cladonia rangiferina (L.) Hoffmann, from Feuerbach.—Usnic acid.

C. pyxidata (L.) Fries, from Feuerbach.—Parellic acid.

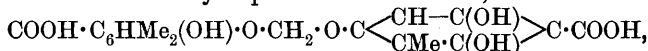
C. coccifera (L.) Schaerer, from Brand in the Vorarlberg.—Coccellic acid.

C. rangiformis, Hoffmann, from Stockheim on Keuper sandstone ("Schilfsandstein"), and from Feuerbach on Keuper marl ("Mergel"); the first sample gave twice as large a yield as the second.—Atranorin, rangiformic acid, and atranorinic acid; further, a wax which melts at 81° and has the composition $C_{28}H_{54}O_2$. Rangiformic acid, $C_{20}H_{35}O_5 \cdot OMe$, sometimes crystallises with $2H_2O$; it is a dibasic acid; the *potassium*, *barium*, *calcium*, *copper*, *lead*, and *silver* salts, with 0, 2, $1\frac{1}{2}$, $1\frac{1}{2}$, 2, and 0 H_2O were prepared and analysed. When treated with hydriodic acid, it yields *norrangiformic acid*, $C_{18}H_{31}(COOH)_3$, of which

it is the monomethylic salt; this acid crystallises with $2\text{H}_2\text{O}$, of which it loses 1 in a desiccator, and then melts at 119° . Atranorin (atranoric acid, Paternò and Oglialoro), probably



is decomposed by heating with acetic acid at 150° , the products being, beside a resin, physciol and methylic betorcinolcarboxylate, $\text{COOMe} \cdot \text{C}_6\text{HMe}_2(\text{OH})_2$; of these, the former dissolves more rapidly in boiling water. Physciol (atranorinic acid, Paternò), probably $\text{C}_6\text{H}_2\text{Me}(\text{OH})_3$ [1:2:4:6], when heated with acetic anhydride at 85° , forms an oily *monacetyl* derivative, from which a very small quantity of crystals, melting at 78° , separated; both of these substances give a purple-violet coloration with ferric chloride. When boiled with acetic anhydride and sodium acetate, it yields a product which is separated by boiling with water into an insoluble oil and crystals which melt at $80\text{--}82^\circ$ and have the composition $\text{C}_{11}\text{H}_{10}\text{O}_4$. Methylic betorcinolcarboxylate (physcianin, atraric acid, ceratophyllin) yields carbonic anhydride and β -orcinol when it is heated with hydriodic acid; it greatly resembles its next lower homologue, methylic orsellinate, and, like it, gives a blood-red coloration with bleaching-powder solution. Theoretically, the hydrolysis of atranorin ought to yield, in addition to physciol and methylic betorcinolcarboxylate, formaldehyde and carbonic anhydride; it was not found possible to demonstrate the formation of formaldehyde, however. The final products of hydrolysis with baryta are methylic alcohol, physciol, β -orcinol, carbonic anhydride, and a little resin (polymerised formaldehyde?). When atranorin is heated with methylic, ethylic, or isoamylic alcohol at 150° , the products are methylic betorcinolcarboxylate and methylic, ethylic, or *isoamylic* hæmatommate, $\text{CH}_2 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{C}_6\text{HMe}(\text{OH}) \cdot \text{COOR}$ [$= 4:6:1:2:3$], the last of these melts at 54° , and gives a dark brown coloration with ferric chloride; the first two were named respectively hæmatomminic and hæmatommic acid by Zopf. Atranorinic acid,



crystallises with $1\text{H}_2\text{O}$, melts at 157° when anhydrous, gives a dark-brown coloration with ferric chloride, and is decomposed, when heated with alcohol at 150° , into physciol, β -orcinol, and carbonic anhydride.

Cetraria islandica (L.) Ach., purchased in Stuttgart and Frankfurt. —Lichenostearic acid and protocetraric acid, the second of which is dissolved out but very slowly by the ether; cetraric acid does not exist ready formed in the lichen. Lichenostearic acid, $\text{OH} \cdot \text{C}_{16}\text{H}_{26}\text{O} \cdot \text{COOH}$, melts at 120° , its *monacetyl* derivative at 124° ; the *barium*, sometimes with $3\text{H}_2\text{O}$, and *silver* salts were prepared and analysed. *Protocetraric acid*, $\text{C}_{30}\text{H}_{22}\text{O}_{15}$, often crystallises with $1\text{H}_2\text{O}$; it decomposes at $240\text{--}260^\circ$ without melting, and although a very insoluble substance, has a very bitter taste; it gives a brownish-to claret-red coloration with ferric chloride. It contains no methoxyl group, and is hydrolysed by boiling with alcoholic potash, or with milk of lime, yielding fumaric and cetraric acids. (Usnaric acid, mentioned above, is isomeric with protocetraric acid, and behaves similarly when heated; it is perhaps

capable of hydrolysis to maleic and cetraric acids). Cetraric acid, $C_{26}H_{20}O_{12}$, has also a very bitter taste, and gives a brownish-red to purple coloration with ferric chloride; its *barium* salt was prepared and analysed.

C. juniperina (L.) Ach.—Chrysocetraric, usnic, and vulpic acids.

C. pinastri (Scop.) Ach., from Berchtesgaden, Brand in the Vorarlberg, and Baden.—Chrysocetraric, usnic, and vulpic acids; the last two differ in composition only by the elements of water. Chrysocetraric acid (perhaps $COOMe \cdot CPh : C \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} C : CPh \cdot COOH$, as it resembles vulpic acid in its reactions, is yellow), and melts at $196-198^{\circ}$ (not 178°); its yellow *potassium*, *barium*, *calcium*, and *lead* salts, with 0 or 3, 0, 4 and 2 H_2O respectively, were prepared and analysed; its yellow *ethylic* salt, from the potassium salt and alcoholic ethylic iodide at 150° , melts at 146° , its yellow monacetyl and *monobenzoyl* derivatives at $163-164^{\circ}$ and 156° ; when boiled with aqueous baryta, it yields *oxypulvic acid*, $C_{18}H_{12}O_6$. This acid is orange-red, or lighter, in colour according as it is crystallised with 2 or $1H_2O$; it melts at 207° when anhydrous; its *barium* salt, with $1H_2O$, was prepared. It is a dibasic acid, being, in fact, the acid of which chrysocetraric acid is the monomethylic salt. If boiled with acetic anhydride, it forms a yellow *anhydride* melting at 196° , and when this is boiled with methylic alcohol, the monomethylic salt (chrysocetraric acid) is first formed, and then the yellow dimethylic salt which melts at 117° ; when oxypulvic acid is boiled with ethylic alcohol, a yellow *monethylic* salt, melting at 139° , homologous with chrysocetraric acid, is first formed, but is rapidly converted into the *diethylic* salt, which is also yellow and melts at 100° . Vulpic acid, $C_{18}H_{11}O_4 \cdot OMe$, yields methylic alcohol and pulvic acid when boiled with aqueous baryta; the last acid, when heated with acetic anhydride, forms a yellow *anhydride* which melts at $214-215^{\circ}$ (after crystallisation from benzene at $220-221^{\circ}$), and is converted into pulvic acid when it is boiled with acetic acid, into vulpic acid when heated with methylic alcohol.

C. F. B.

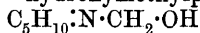
Guarana Paste. By E. KIRMSSE (*Arch. Pharm.*, 1898, 236, 122—141. Compare Schaer, *ibid.*, 1890, 228).—From guarana paste, the author has obtained the guarana tannin by extracting (1) with hot water, or (2) with alcohol at the ordinary temperature, or (3) with ether of sp. gr. = 0.750; it forms a yellowish-white, amorphous mass, with an astringent taste, is easily soluble in water, alcohol, ether containing alcohol, and in ethylic acetate, and partly soluble in absolute ether. The product obtained by the second method has a reddish tint, due to partial decomposition. By extracting the crude tannin with ether, crystals of a catechin are obtained whose properties and reactions are identical with those of the catechin of Pegu-catechin. After drying over sulphuric acid for several weeks, its analysis showed a composition corresponding with Neubauer's formula, $C_{17}H_{24}O_{10}$, and it melted at 140° ; but after cooling, powdering, and drying at $150-160^{\circ}$ it melted at 190° when again heated, intumescing and acquiring the characteristic colour of guarana. When dried at $80-90^{\circ}$ and at 98° , the percentage of carbon increased to a mean of

62.20 and 63.08 per cent. respectively. The product obtained by extracting the paste with hot water contains the least amount of catechin. The author confirms Thoms' statement (*Pharm. Centralhalle*, 1890, 533) that the amount of caffeine in guarana has been overestimated; three samples were found to contain 2.68, 2.97, and 3.10 per cent. respectively. Cocoa, which has been stated to be an adulterant of lower qualities of guarana, was not detected in any of the samples.

E. W. W.

Chemistry of Chlorophyll. By LEO MARCHLEWSKI (*J. pr. Chem.*, [ii], 57, 330—334).—A very destructive criticism of Bode's paper (*Inaug. Diss.*, Cassel, 1898).

Action of Hydrogen Peroxide on 1-Alkylpiperidine Bases. By W. WERNICK and RICHARD WOLFFENSTEIN (*Ber.*, 1898, 31, 1553—1561).—Merling's "hydroxymethylpiperidine,"



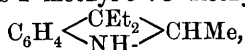
(*Abstr.*, 1893, i, 113), obtained by the action of hydrogen peroxide on 1-methylpiperidine, must rather be regarded as *methylpiperidine oxide*, $\text{C}_5\text{H}_{10}:\text{NMe}:\text{O}$, its hydriodide being $\text{C}_5\text{H}_{10}:\text{NMeI}\cdot\text{OH}$, for when it is heated at 200° with hydrochloric acid saturated at 0° , it forms 1-methylpiperidine, together with a little methylic chloride (the same reaction takes place, but with almost explosive violence, when gaseous hydrogen chloride is passed over the dry substance at 180 — 230°); it reacts neither with benzoic nor with benzenesulphonic chloride; it is reduced by sulphurous acid, nitrous acid, or zinc and hydrochloric acid to 1-methylpiperidine; it loses oxygen with explosive violence when submitted to dry distillation, 1-methylpiperidine being formed; and it sets free iodine from potassium iodide (although its salts do not effect this).

Ethylpiperidine oxide, $\text{C}_5\text{H}_{10}:\text{NEt}:\text{O}$, obtained by allowing 1-ethylpiperidine to remain at the ordinary temperature with the calculated quantity of 3 per cent. hydrogen peroxide solution, forms hygroscopic crystals. The yellow *picrate* melts at 142 — 144° ; the *hydrobromide* and the *hydriodides*, with $\frac{1}{2}\text{HI}$, melting at 95° , and with 1HI , deliquescent, were prepared and analysed. In its reactions, this substance resembles the methyl analogue, except that when submitted to dry distillation it decomposes for the greater part into ethylene and δ -amidovaleraldehyde, $\text{NH}_2\cdot[\text{CH}_2]_4\cdot\text{CHO}$, although some ethylpiperidine is formed.

C. F. B.

The Methylation of Indoles. By GIUSEPPE PLANCHER (*Ber.*, 1898, 31, 1488—1499. Compare Brunner, this vol., i, 384).—When the base $\text{C}_{13}\text{H}_{17}\text{N}$, obtained by the action of ethylic iodide on 2'-methylindole (*Abstr.*, 1897, i, 102) is oxidised with potassium permanganate, it yields an acid, $\text{C}_{13}\text{H}_{15}\text{NO}_2$, which, when it loses carbonic anhydride, is converted into the substance $\text{C}_6\text{H}_4\langle\text{C}_{\text{Et}}\text{N}\rangle\text{CH}$, for which the name 3':3'-diethylindolenine is proposed; consequently the formula of the acid must have been $\text{C}_6\text{H}_4\langle\text{C}_{\text{Et}}\text{N}\rangle\text{C}\cdot\text{COOH}$, and

that of the original base $C_6H_4 \begin{smallmatrix} \text{CEt}_2 \\ \text{---N} \end{smallmatrix} \gg CMe$, the base being not 4:4'-diethyl-dihydroquinoline, as has been assumed hitherto, but 2-methyl-3':3'-diethylindolenine. This base is reduced by sodium to another, of which the hydrochloride melts at 217° (*loc. cit.*, p. 103); this is to be regarded as 2'-methyl-3':3'-diethylindoline,



not 4':4'-diethyltetrahydroquinoline; from it, the first base can be regenerated by oxidation with alkaline potassium permanganate at 0° . In the same way, Ferratini's dimethyltetrahydroquinoline (*Abstr.*, 1893, i, 603), better 2':3':3'-trimethylindoline, can be oxidised to 2':3':3'-trimethylindolenine (4:4'-dimethyldihydroquinoline), the yellow *picrate* of which melts at 158° . This base can also be prepared by heating the phenylhydrazone of methyl isopropyl ketone (which boils at $175\text{--}176^\circ$ under 47 mm. pressure) with alcoholic zinc chloride on the water bath; it boils at $228\text{--}229^\circ$ under 744 mm. pressure, and the *zincchloride* melts at 225° . This method of formation confirms the view that the substance is an indolenine rather than a dihydroquinoline; it might be urged that a quinoline chain is formed during the reaction by the migration of a methyl group, but this objection is met by the fact that in a case where no such migration is possible, namely, that of the phenylhydrazone of di-isopropyl ketone, a similar condensation occurs on heating with zinc chloride, a base being formed which boils at $250\text{--}260^\circ$ under 750 mm. pressure, melts at 80° , and must be regarded as 3':3'-dimethyl-2'-isopropylindolenine.

When 2':3':3'-trimethylindolenine, $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{---N} \end{smallmatrix} \gg CMe$, is treated with methylic iodide, the product is the hydriodide of 1':3':3'-trimethyl-2'-methyleineindoline, $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{---NMe} \end{smallmatrix} \gg CMeI$, from which the free base, $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{---NMe} \end{smallmatrix} \gg C:CH_2$ (trimethyldihydroquinoline, E. Fischer and Steche, *Abstr.*, 1888, 298) can be set free with potash. The same base is obtained by condensing the methylphenylhydrazone of methyl isopropyl ketone (which boils at $130\text{--}140^\circ$ under 40 mm. pressure) by means of zinc chloride. In a similar fashion, the hydriodide of 1':3':3'-trimethyl-2'-isopropylideneindoline (pentamethyldihydroquinoline: Zatti and Ferratini, *Abstr.*, 1892, 615) is obtained from 2'-isopropyl-3':3'-dimethylindolenine and methylic iodide; it melts at 185° (not 173°), the aurochloride at about 150° , and the *picrate* at 148° .

C. F. B.

Ketochlorides and Orthodiketones of Azimidobenzene. By THEODOR ZINCKE (*J. pr. Chem.*, 1898, [ii], 57, 319—329).—This paper discusses the results of experimental work previously published. It has been already shown (*Abstr.*, 1896, i, 499, 501) that the carbon ring of quinoline reacts in many cases just like one of the two rings in naphthalene; it is now shown that the same is true of the carbon ring in azimidobenzene, except that it is not possible to convert the six-atom into a five-atom carbon ring.

C. F. B.

Cycloamidines : Pyrimidine Derivatives. By HENRY LORD WHEELER (*Amer. Chem. J.*, 1898, 20, 481—490).—The author gives the name of cycloamidines to those substances having the amidine constitution $\text{NXR}^1\cdot\text{CR}^1\cdot\text{NR}^1$, but which have two of the radicles R, R^1 , and R^1 replaced by a ring structure or a bivalent group.

When R^1 and R^1 are thus replaced, cycloamidines are formed containing two nitrogen atoms in the ring, and a preliminary account of the action of alkylic haloids on compounds of this series is given in the paper. The action of alkyl haloids on cycloamidines containing only one nitrogen atom in the ring has been extensively studied, and many cases have been found in which substitution of the hydrogen atom X does not take place. 4:2:6-Anilidophenylmethylpyrimidine,

$\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{CH} \\ \text{CPh} \text{---} \text{N} \end{smallmatrix} \text{C}\cdot\text{NHPh}$, a cycloamide containing two nitrogen

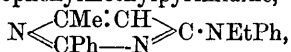
atoms in the ring, behaves in a similar manner, forming stable additive products with alkylic iodides from which the original base is regenerated on treatment with dilute alkali. This cycloamide is prepared from 4:2:6-chlorophenylmethylpyrimidine and aniline, yields a *hydrobromide* melting at 250° and a *hydriodide* melting at 231° ; both salts form colourless needles; the *methiodide*, $\text{C}_{18}\text{H}_{18}\text{N}_2\text{I}$, crystallises from dilute alcohol in colourless needles containing $2\text{H}_2\text{O}$; and becomes anhydrous at 130° . Dilute alkalis reconvert it into the original cycloamide. 4:2:6-Methylanilidophenylmethylpyrimidine,

$\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{CH} \\ \text{CPh} \text{---} \text{N} \end{smallmatrix} \text{C}\cdot\text{NMePh}$, prepared from phenylmethylchloropyrimidine and methylaniline, crystallises in colourless prisms and melts

at 113° ; the *platinochloride* decomposes at 228° , the *hydriodide* melts at 198° , and the *nitrate* crystallises in colourless needles or prisms and decomposes at about 170° .

4:2:6-Anilidophenylmethylpyrimidine *ethiodide*, $\text{C}_{19}\text{H}_{20}\text{N}_2\text{I} + 2\text{H}_2\text{O}$, is crystalline, and becomes anhydrous at 130° . Dilute alkalis regenerate the original cycloamide.

4:2:6-Ethylanilidophenylmethylpyrimidine,



prepared like the corresponding methyl derivative, crystallises in colourless prisms soluble in alcohol but not in water, and melts at 87° ; the *hydrochloride* melts at 210° , and the *platinochloride* at 218° ; the *hydriodide* crystallises in prisms. Ethylic bromide is without action on anilidophenylmethylpyrimidine.

2:6:4-Phenylmethylpyrimidinomethiodide, produced by heating phenylmethoxyypyrimidine, $\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{CH} \\ \text{CPh}\cdot\text{NH} \end{smallmatrix} \text{CO}$, and methylic iodide

at 170° , crystallises from alcohol in colourless needles and decomposes at 230° . When treated with dilute alkali, the methiodide loses the elements of hydrogen iodide and 2-phenyl-1(or 3):6-dimethylpyrimidone, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}$, is obtained, which crystallises from water in large prisms and melts at $91\text{--}92^\circ$; it is basic in character, and yields soluble salts with dilute acids. The *nitrate* forms colourless, flattened prisms and melts at 195° ; the *platinochloride* crystallises in orange-red prisms and darkens at 235° .

Methylbenzamidine hydrochloride, $\text{NH}\cdot\text{CPh}\cdot\text{NHMe}\cdot\text{HCl}$, prepared from the hydrochloride of benzimidioethylic ether and methylamine, crystallises from water in colourless needles. G. T. M.

A New Product of the Oxidation of Theobromine. By HANS CLEMM (*Ber.*, 1898, 31, 1450—1453).—When theobromine is suspended in dilute hydrochloric acid, warmed to 40—50°, and oxidised with potassium chlorate, methylalloxan is the chief product (this vol., i, 178), but a second product, melting and decomposing at 201—203°, is formed in addition; this is an *oxy-3:7-dimethyluric acid*, for it is hydrolysed by aqueous baryta to methylcarbamide and mesoxalic acid; it is soluble in alkalis, but not in acids. When heated with water for an hour at 100°, it is converted into an isomeride, *iso-oxy-3:7-dimethyluric acid*, which also melts and decomposes at 201—203°, and yields the same products when hydrolysed with baryta, but is much more soluble in water than the compound first mentioned; it forms monoclinic crystals [$a:b:c=0.7908:1:1.2092$; $\beta=83^\circ 9' 20''$]. The structure of these two compounds is not quite evident. C. F. B.

Pseudotheobromine, Theobromine, Theophylline, and Paraxanthine. By HERBERT POMMERHNE (*Arch. Pharm.*, 1898, 236, 105—122).—From the products of the action of methylic iodide on the silver derivative of xanthine at 130—140°, the author has isolated xanthine, theobromine, and pseudotheobromine (compare Abstr., 1897, i, 129). Pseudotheobromine, when treated with methylic iodide, yields caffeine. The author has prepared the following salts of theophylline obtained from tea-extract, and of paraxanthine. Theophylline hydrochloride, $\text{C}_7\text{H}_8\text{N}_4\text{O}_2\cdot\text{HCl} + \text{H}_2\text{O}$, crystallises in plates, loses its water and hydrochloric acid at 100°, is more soluble in water than either the hydrochloride of theobromine or of pseudotheobromine, and forms a strongly acid solution. The aurochloride, $\text{C}_7\text{H}_8\text{N}_4\text{O}_2\cdot\text{HAuCl}_4 + \text{H}_2\text{O}$, crystallises in lemon-yellow needles, is easily soluble in water, loses its water of crystallisation at 110°, and does not melt below 285°; the corresponding salt of pseudotheobromine melts at 270°. *Theophylline platinochloride*, $(\text{C}_7\text{H}_8\text{N}_4\text{O}_2)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in small plates, is easily soluble in water, and does not melt below 280°; pseudotheobromine platinochloride crystallises with $4\text{H}_2\text{O}$. Paraxanthine hydrochloride, $\text{C}_7\text{H}_8\text{N}_4\text{O}_2\cdot\text{HCl} + \text{H}_2\text{O}$, crystallises in characteristic, transparent, rhombic plates, is easily soluble in water, forming a strongly acid solution, very easily soluble in hydrochloric acid, and loses its halogen acid and water at 100°; the *aurochloride*, $\text{C}_7\text{H}_8\text{N}_4\text{O}_2\cdot\text{HAuCl}_4 + \frac{1}{2}\text{H}_2\text{O}$, crystallises in orange-yellow needles, melts at 227—228°, is sparingly soluble in cold water, more soluble in hot, and loses its water of crystallisation at 100°; the *platinochloride*, $(\text{C}_7\text{H}_8\text{N}_4\text{O}_2)_2\cdot\text{H}_2\text{PtCl}_6$, forms small, reddish-yellow needles, and does not melt below 290°. E. W. W.

Quinoline-morphine. By PAUL COHN (*Monatsh.*, 1898, 19, 106—113. Compare Abstr., 1897, i, 170).—*2-Quinoline-morphine*, $\text{C}_9\text{NH}_6\cdot\text{O}\cdot\text{C}_{17}\text{H}_{17}\text{NO}\cdot\text{OH}$, prepared by the action of 2-chloroquinoline on morphine, crystallises from alcohol in star-like groups of small

prisms melting at 158°. Unlike morphine, it is insoluble in alkalis, and gives no colour reaction with ferric chloride. With bromine, it yields a substitution product, and with iodine a periodide. It forms both normal and acid salts, the latter being amorphous. The normal *hydrochloride* is a hard mass crystallising with difficulty; the *platino-chloride* is a pale yellow precipitate, decomposing without melting at 180—190°; the normal *sulphate* crystallises from water in slender, glistening needles, melting and giving off gas at 257°, and has a specific rotation $[\alpha]_D = -66.46^\circ$; the *chromate* is obtained as a yellow precipitate; the *tartrate* separates from alcohol in beautiful, transparent, glistening prisms, melting and giving off gas at 98°, whilst the *picrate* forms small, yellow crystals, melting and decomposing at 250—252°.

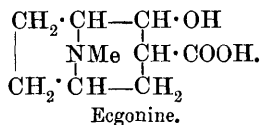
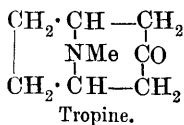
The normal sulphate is a strong poison, 0.001—0.002 gram producing death in cold-blooded, and 0.02 gram in warm-blooded animals. It produces clonic spasms, lessens the blood pressure, and retards the action of the pulse.

It was found impossible to replace the hydrogen atom of the second hydroxyl group in morphine by a quinoline residue. A. W. C.

Tropic Acid. III. Constitution of the Products of Decomposition of Atropine and Cocaine. By RICHARD WILLSTÄTTER (*Ber.*, 1898, 31, 1534—1553. Compare also this vol., i, 159).—When piperylenedicarboxylic acid (*Abstr.*, 1896, i, 266) is reduced with sodium amalgam in aqueous solution at 100°, pimelic acid, $\text{COOH} \cdot [\text{CH}_2]_5 \cdot \text{COOH}$, is obtained. A second product, more readily soluble in cold water, is obtained in addition; this, which is a *dihydro-piperylenedicarboxylic acid*, perhaps $\text{COOH} \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_3 \cdot \text{COOH}$, melts at 120—121°, its *dibromide* (*dibromopimelic acid*) at 140°. When carbonic anhydride is passed through the solution during the reduction, no pimelic acid is formed, but only a *dihydropiperylenedicarboxylic acid*, isomeric with the first, however, and possibly of the constitution $\text{COOH} \cdot [\text{CH}_2]_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$; this acid melts at 91°, but not sharply; the *dibromide* melts at 130°. When piperylenedicarboxylic acid is heated with hydriodic acid at 170—180°, it is converted into a lactone-acid, probably the *γ-hydroxypimelic acid lactone*, $\text{COOH} \cdot [\text{CH}_2]_2 \cdot \text{CH} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CO}$; this melts at 82.5°, and has the electrolytic dissociation constant $K = 0.00272$ ($\mu_\infty = 376$); its silver salt is very readily soluble in water; that of the hydroxypimelic acid is less soluble, and was analysed.

The formation of normal pimelic acid by the addition of four hydrogen atoms to piperylenedicarboxylic acid makes it necessary to regard the latter as a normal acid, contrary to the view previously taken; it is probably $\text{COOH} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$, although the position of the double bonds is not certain. And as this acid is obtained from methylic *i*- or *d*-tropate (by the addition of methylic iodide and treatment with potash alternately), and the optically isomeric tropic acids are obtained by the oxidation of tropine or ecgonine (with chromic and sulphuric acids), the formulæ proposed by Merling for these alkaloids, and hitherto adopted by the author, must be given up,

and the following assigned instead (in that of ecgonine the $\text{CH}\cdot\text{OH}$ and $\text{CH}\cdot\text{COOH}$ groups may be interchanged, and in any case ecgonine is not the acid, but its betaine, or intramolecular salt).



The formulæ of a number of products of the decomposition of these alkaloids are deduced; that of tropic acid, for example, is $\text{CH}_2 - \text{CH}(\text{COOH}) - \text{CH}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{COOH}) > \text{NMe}$. It is impossible to reproduce this part of the paper in an abstract; the original must be consulted.

C. F. B.

Pilocarpidine. By C. EMANUEL MERCK (*Arch. Pharm.*, 1898, 236, 141—149. Compare this vol., i, 283).—According to the author, Petit and Polonowsky's method of converting pilocarpine into pilocarpidine by heating the hydrochloride at 200° (Abstr., 1897, i, 581 and 583) does not affect the composition of the salt, although its rotatory power is diminished. When pilocarpidine hydrochloride is similarly treated, a product is obtained which has a lower rotatory power than the original hydrochloride. In aqueous solution, it yields a platinochloride melting at 184 — 186° , and whose content of platinum corresponds with the formula $(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2)_2 \cdot \text{H}_2\text{PtCl}_6$; from the mother liquor, small, apparently cubic, crystals of a platinochloride $(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2)_2 \cdot \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ separate. Neither by heating pilocarpine with hydrochloric acid in aqueous solution, nor by boiling it with water according to Hardy and Calmels' methods, could pilocarpidine be obtained; in each case, there was a diminution of rotatory power, but no change in composition.

E. W. W.

Hydrolysis of Proteids. By A. EICHHOLZ (*J. Physiol.*, 1898, 23, 163—177).—From white of egg three substances can be separated, each capable of yielding an osazone corresponding with phenyl-glucosazone; they are, in order of solubility, ovo-mucoid, egg-albumin, ovo-mucin. The last-named substance has not been previously described.

Pure serum-albumin yields no osazone, and the glucoproteid reaction of the mixed serum proteids depends on a portion of the globulin which can be precipitated by the addition of acetic acid to dilute serum. Casein after hydrolysis also yields no osazone. Such experiments show the importance and wide distribution of glucoproteids; all proteids, however, are not glucoproteids.

W. D. H.

Uroproteic Acid, a New Constituent of Urine. By MAX CLOETTA (*Chem. Centr.*, 1897, ii, 1154; from *Arch. exp. Path. Pharm.*, 40, 29—39. Compare Töpfer, this vol., ii, 501).—To prepare uroproteic acid, dogs' urine is treated with calcium carbonate or baryta, the excess of the base removed by sulphuric acid or carbonic anhydride,

the filtrate made neutral or slightly alkaline, evaporated to a syrup, warmed with excess of barium hydroxide, and then treated with four times its volume of 95 per cent. alcohol. The coarse, flocculent, yellowish-brown precipitate of the basic barium salt thus obtained is filtered, washed with water, decomposed with sulphuric acid, the solution neutralised with barium carbonate, decolorised with animal charcoal, evaporated to a small volume, and treated with alcohol. Two grams of the barium salt was obtained from 4 litres of the urine of dogs which had been well fed on flesh. The formula of the acid deduced from analysis of the barium salt is probably $C_{66}H_{116}N_{20}SO_{54} + nH_2O$. This acid is a derivative of albumin, and does not give the biuret reaction. When decomposed with sulphuric acid, it yields a melanin-like substance, *uromelanin*, formic acid, carbonic acid, and ammonia.

E. W. W.

Cytological Staining. By ALBERT MATHEWS (*Amer. J. Physiol.*, 1898, 1, 445—454).—The acid histological stains will combine with albumoses only in acid solutions; under such circumstances, they form combinations similar to picric or other acid combinations with albumoses, and probably enter into one or more of the amido-groups in the albumose molecule. The basic stains will combine with albumoses only in alkaline solution, when they form insoluble, coloured compounds. The basic dyes react in this respect like basic lead acetate, protamine, histon, or other organic bases. The basic stains probably enter the hydroxyl of the phenol group of the albumose molecule, since they will not precipitate gelatin.

The staining of coagulated egg-albumin depends on chemical combinations similar in all respects to those which the albumoses enter into with the same stains. Freshly prepared hæmatoxylin will not stain tissues and, corresponding with this, will not precipitate the albumoses in either acid, neutral, or alkaline solutions. Hæmatein and sodium carminate react towards the albumoses and tissues like the acid stains. The aluminium salts of these stains, however, probably owing to the strong basicity of the metal, react like basic stains.

The affinity of microscopic sections for stains depends on reactions similar to the above. In slightly acid or neutral solutions, the basic dyes will stain any element of the tissue which contains an organic acid in a saline combination with a strong base; hence their affinity for the chromatin of nuclei, in which a histon or protamine salt of nucleic acid is contained. Artificial nucleins are also stained by methyl-green so long as they are not saturated with albumin; as soon as the acid becomes saturated with albumin, the nuclein shows a preponderating attraction for acid stains. This is evidence that the acid stain enters the albumin molecule, whilst the basic enters the nucleic acid molecule in these nucleins.

W. D. H.

Hæmin Hydrochloride. By MAX ROSENFELD (*Chem. Centr.*, 1897, ii, 1153; from *Arch. exp. Path. Pharm.*, 40, 137—146).—According to the author, the composition of hæmin prepared from horses' blood by Cloetta's method (*Abstr.*, 1896, i, 660) differs from that prepared by Cloetta from the blood of oxen only in containing 0.5 per cent. less of

hydrogen. When Nencki's method (Abstr., 1895, 69, 825) is modified so that the blood-powder is prepared by diluting with sodium sulphate solution before centrifugalising, a product whose content of nitrogen corresponds with Cloetta's formula, $C_{30}H_{34}N_3FeO_3$, is obtained. Hence the author assumes that Nencki's preparation contains a substance rich in nitrogen, and since phosphorus could be detected (by molybdate after fusing with sodium carbonate and potassium nitrate), this substance is probably nuclein derived from the colourless blood corpuscles. Hæmin, containing 3 atoms of nitrogen to 1 of iron, can be prepared as follows. Fresh oxen blood, after removing the fibrin, is mixed with a 2 per cent. solution of sodium sulphate and centrifugalised; the mass of corpuscles is freed from serum, again treated with sodium sulphate, centrifugalised, and then mixed with twice its volume of 96 per cent. alcohol, filtered after remaining 1—2 hours, and dried at the ordinary temperature. A solution of anhydrous oxalic acid in alcohol is added to 300—400 grams of the powder mixed with sufficient 96 per cent. alcohol to form a thin pulp, until the colour changes from red to brown. The filtrate, after remaining 24 hours, is again filtered, and a concentrated solution of hydrogen chloride in alcohol added drop by drop; the hæmin crystals, which at once begin to separate, are washed with alcohol, ether, and water, and then recrystallised from hot alcohol to which a solution of hydrogen chloride in alcohol is added. The content of chlorine is not constant, and the chlorine cannot be completely removed by washing with water. E. W. W.

Iodine in the Thyroid Gland. By R. TAMBACH (*Zeit. Biol.*, 1898, 36, 549—567).—The absolute quantity of iodine in the thyroids of pigs from different sources is fairly constant, but the amount of proteids that can be extracted varies considerably. The iodine-containing proteid compounds are almost completely extractable with water. These compounds are precipitable by reagents like acids, alcohol, &c., which precipitate proteids; only a small percentage (4) of the total iodine remains in solution; of this, half is present in compounds soluble in water, such as iodides; the remaining half is more firmly combined, but these combinations are also soluble in water. There is no free iodothylin in the gland. By artificial gastric and pancreatic digestion of the iodine proteid compounds, iodothylin is not separated, but digestive products are formed in which the iodine is combined in a similar way to that in which it is in the parent substance. Iodothylin is only obtainable by destruction of the proteid molecule, and even then all the iodine is not present as iodothylin; part passes into a peptone-like substance. The iodine, in fact, appears to be present in the form of several proteid compounds. The therapeutic activity of extracts of the thyroid is more probably associated with these proteid compounds of iodine or their digestive products than with iodothylin.

W. D. H.

Iodothylin. By ERNST ROOS (*Zeit. physiol. Chem.*, 1898, 25, 1—15).—The following elementary analyses of iodothylin are given in percentages.

I. From sheep. II. From human thyroids; *a*, from Switzerland, *b*, from Kiel.

	I.	S.	N.	C.	H.	Cl.	Ash.
I.	4·31	1·40	8·91	58·24	7·43	0·4	0·40
II { <i>a</i> .	1·31	1·40	10·41	61·41	8·06	0·52	—
II { <i>b</i> .	2·58	1·40	10·03	57·04	7·28	0·5	0·47

These numbers show great discrepancies, especially in the percentage of iodine, which is particularly abundant in the iodothylin of the sheep. Whether these differences are due to the mode of preparation, or indicate real individual differences between iodothylin from various sources, is still uncertain.

W. D. H.

Organic Chemistry.

Explosion of Mixtures of Methane by Electric Currents. By H. COURIOT and JEAN MEUNIER (*Compt. rend.*, 1898, 126, 750—753).—An extensive series of experiments was made on the action (1) of incandescent wires or filaments, and (2) of electric sparks on mixtures of methane with various proportions of air, the gas being sometimes still and sometimes in motion.

A current of a mixture of 80 per cent. of methane and 20 per cent. of air could not be ignited by an incandescent wire or by the spark produced when the wire melted owing to the intensity of the current. In contact with a flame, however, the mixture readily ignited.

Whatever the proportion of air and methane, the only effect produced by an electric current, if it produces any effect at all, is an explosion. Under no circumstances, however, were the authors able to produce an explosion by means of an incandescent wire. When an explosion is produced, it is due to the breaking of the wire and the consequent production of a spark. The most readily explosive mixture contains 9·5 per cent. of methane. So long as the proportion of methane does not fall below 5·5 per cent., combustion during the explosion is complete. Slight explosions were observed with so low a proportion of methane as 4·5 per cent. The maximum limit of explosibility is 12 per cent. of methane, and the authors never obtained an explosion when the proportion was as high as 12·25 per cent.

C. H. B.

Ignition of Mixtures of Methane and Air by the Electric Spark. By H. COURIOT and J. MEUNIER (*Compt. rend.*, 1898, 126, 901—904).—The authors have previously described experiments which show that mixtures of methane and air are not ignited by incandescent wires, but if the wires fuse and a spark is produced, ignition takes place (preceding abstract). They now find that if the current by which the wire is heated is shunted with a parallel shunt, the production of the spark causes no ignition when the resistances in the two branches are equal. If the resistance of the shunt is high, the production of a spark always leads to the ignition of the mixture of methane and air; on the other hand, when the resistance of the shunt falls below a certain value, the production of a spark likewise causes an explosion. In order to avoid an explosion, the intensity of the current must not exceed a certain maximum, which depends on the resistance of the two branches of the conductor.

C. H. B.

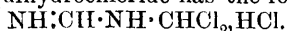
Di-isopropyl in Light Petroleum from Baku. By OSSIAN ASCHAN (*Ber.*, 1898, 31, 1801—1803. Compare this vol., i, 407).—It is shown experimentally that the fraction of Russian petroleum which boils at 57—59° consists of di-isopropyl.

M. O. F.

Combination of Olefines with Mercury Salts. By GEORGES DENIGÈS (*Compt. rend.*, 1898, 126, 1145—1148).—The olefines generally, like butylene, combine with mercuric sulphate in acid solution, and yield compounds of the type $(\text{SO}_4\text{Hg}, \text{HgO})_3\text{R}''$, in which R'' is an olefine; they are yellow compounds which dissolve readily in hydrochloric acid, especially on heating, and with effervescence if the particular olefine is gaseous at the ordinary temperature. A solution of 50 grams of mercuric oxide in 200 c.c. of sulphuric acid and 1000 c.c. of water may conveniently be used. The olefine, if gaseous, is passed into this solution, or if liquid, like trimethylethylene, is agitated with it. All three butylenes yield similar compounds, and that obtained from unsymmetrical dimethylethylene is more stable than the compound formed by trimethylethylene. The propylene compound is very unstable, and at 90—100° in contact with the mother liquor it is rapidly converted into mercuric sulphate and acraldehyde. C. H. B.

Purification of Acetylene. By A. BERGE and ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 218—221).—Acetylene, prepared from commercial calcium carbide, is contaminated with notable quantities of hydrogen sulphide and hydrogen phosphide. Both these impurities may be removed by passing the gas through bromine water, as recommended by Willgerodt, but this reagent rapidly becomes exhausted, is incapable of regeneration, and converts part of the acetylene into bromine derivatives. Hydrogen sulphide is best removed by means of caustic soda solution, and hydrogen phosphide by subsequently passing the gas through a solution of mercuric chloride acidified with hydrochloric acid, or through nitric acid containing a small quantity of a salt of copper or iron in solution. The precipitate produced in the mercuric chloride solution may be collected and dissolved in nitric acid; a little hydrochloric acid is then added, and the solution is ready for further use. By making use of these processes, the impurities may be quantitatively determined, the sulphur absorbed by the caustic soda being converted into sulphuric acid, and the phosphorus into phosphoric acid. Two samples of acetylene were thus found to contain, per cubic metre, 1032 and 1417 c.c. of hydrogen sulphide, and 945 and 985 c.c. of hydrogen phosphide. N. L.

Constitution and Synthetical Application of the Sesquihydrochloride of Hydrogen Cyanide. By LUDWIG GATTERMANN and K. SCHNITZSPAHN (*Ber.*, 1898, 31, 1770—1774).—The authors find that when "sesquihydrochloride of hydrogen cyanide," which was first prepared by Claisen and Matthews (*Ber.*, 1883, 16, 308), who represented it by the formula $2\text{HCN}, 3\text{HCl}$, is heated with benzene, a product is obtained which yields benzhydrylamine, $\text{CHPh}_2 \cdot \text{NH}_2$, on hydrolysis with alcoholic potash. This fact, taken in conjunction with the formation of ethylic chloride, formic acid, and formamidine, when the sesquihydrochloride is heated with alcohol, renders it probable that the so-called sesquihydrochloride has the formula



Benzhydrylformamidine hydrochloride, $\text{NH}:\text{CH} \cdot \text{NH} \cdot \text{CHPh}_2, \text{HCl}$, is prepared by adding aluminium chloride to a mixture of benzene with

the "sesquihydrochloride of hydrogen cyanide," and pouring the product into ice cold water containing a small quantity of hydrochloric acid; the *platinochloride* crystallises from dilute alcohol in yellow needles, and melts at 210° . The free *base* is crystalline, and melts at $118-120^{\circ}$; boiling, dilute caustic soda slowly eliminates ammonia, yielding formylbenzhydramine (Leuckart and Bach, Abstr., 1886, 1023), from which the base is obtained by the prolonged action of alkali.

The "sesquihydrochloride of hydrogen cyanide" acts still more vigorously on toluene, and the product yields tolhydramine (Goldschmidt and Stöcker, Abstr., 1891, 1479). Hexamethyltriamidotriphenylmethane, the leuco-base of "crystal-violet," is obtained by heating dimethylaniline with the "sesquihydrochloride of hydrogen cyanide" at $120-130^{\circ}$ during 3 hours. M. O. F.

Preparation of Cyanogen Chloride. By ALFRED HELD (*Bull. Soc. Chim.*, 1897, [iii], 17, 287—290).—Numerous attempts to devise a more satisfactory method of preparing cyanogen chloride than that of saturating a solution of mercuric cyanide with chlorine, led to the adoption of the following process:—260 grams of potassium cyanide (after allowing for impurity) and 90 grams of crystallised zinc sulphate are dissolved in 8 litres of water, and chlorine is passed into the solution until the white precipitate of zinc cyanide, which is produced in the later stages of the operation, is nearly redissolved. If excess of chlorine has been used, it may be removed by adding a little potassium cyanide. The chlorine is rapidly absorbed, and the solution keeps well for a long time; it may be used immediately after being made, and there is no excess of chlorine to be got rid of, as in the usual process. Each litre of the solution contains at least 30 grams of cyanogen chloride. N. L.

Ammonio-compounds of Cuprosocupric Cyanide. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, 236, 246—248. Compare next abstract).—Twenty years ago, the author made the observation that when an ammoniacal solution of copper sulphate is nearly decolorised by adding potassium cyanide, and allowed to stand, deep green crystals of the composition $\text{Cu}_3(\text{CN})_4 \cdot 3\text{NH}_3$ separate. Denner assigned the same composition to a preparation made in a similar manner in the Marburg laboratory in 1884. Malmberg's results (see next abstract) show that a whole series of green cuprosocupric cyanide compounds, mentioned in literature, and to which various formulæ are assigned, possess in reality the same composition. The above-mentioned green ammonium compound of cuprosocupric cyanide takes up ammonia to form the blue *compound*, $\text{Cu}_3(\text{CN})_4 \cdot 4\text{NH}_3$, and by loss of ammonia is converted into a violet *salt*, $\text{Cu}_3(\text{CN})_4 \cdot 2\text{NH}_3$.

Under the same conditions as above, an ammoniacal nickel sulphate solution gives a violet-coloured salt. A. W. C.

Ammonio-cuprosocupric Cyanide. By EDWARD MALMBERG (*Arch. Pharm.*, 1898, 236, 248—260. Compare preceding abstract).—The following analytical methods were used in this research. Copper was estimated partially as the sulphide by precipitation with hydrogen sulphide, and partially as the metal by heating the substance in an

atmosphere of hydrogen. For the estimation of cyanogen, the compound was distilled with dilute hydrochloric acid, and the liberated hydrogen cyanide received in dilute caustic soda solution and titrated with N/10 silver nitrate solution.

The ammonia was determined by distilling the substance with caustic soda, after addition of sodium sulphide to combine with the cyanogen. The distillate was collected in N/10 sulphuric acid, and after passing carbonic anhydride through the warmed solution to get rid of hydrogen sulphide, the excess of acid was titrated with N/10 caustic potash, using rosolic acid as indicator.

Green Ammonio-cuprosocupric Cyanide Compounds.—The green compounds obtained by Hilkenkamp (*Ann.*, 1859, **97**, 218) of the supposed composition $\text{Cu}(\text{CN})_2 + 2\text{Cu}_2(\text{CN})_2 + 4\text{NH}_3 + 2\text{H}_2\text{O}$; by Dufau (*J. pr. Chem.*, 1853, **59**, 498) of the composition $\text{Cu}_2(\text{CN})_2 + \text{Cu}(\text{CN})_2 + 4\text{NH}_3$; by Schiff and Bechi (*Ann.*, 1866, **138**, 24) of the composition $\text{Cu}(\text{CN})_2 + 2\text{Cu}_2(\text{CN})_2 + 6\text{NH}_3$; and by Fleurent (*Compt. rend.*, 1892, **114**, 1066) of the composition $\text{Cu}_2(\text{CN})_2 + 2\text{Cu}(\text{CN})_2 + 2\text{NH}_3 + 3\text{H}_2\text{O}$, are in reality all represented by the formula $\text{Cu}_3(\text{CN})_4 \cdot 3\text{NH}_3$.

Violet ammonio-cuprosocupric cyanide, $\text{Cu}_3(\text{CN})_4 \cdot 2\text{NH}_3$, is obtained by boiling the finely powdered green salt with water, or with water and a little ammonia, until a sample of the filtered mixture deposits violet crystals. This salt is not decomposed on exposure to the air.

Blue ammonio-cuprosocupric cyanide, $\text{Cu}_3(\text{CN})_4 \cdot 4\text{NH}_3$, is produced when the green salt is heated for some hours on the water bath with a mixture of solutions of ammonia and ammonium carbonate; it is less stable than the violet salt. The blue salts described by Hilkenkamp (*loc. cit.*), Dufau (*loc. cit.*), Fleurent (*loc. cit.*), Schiff and Bechi (*loc. cit.*), and Mills (*Chem. Centr.*, 1863, 154) have also this same composition.

Ammonio-cuprous Cyanide, $\text{Cu}_2(\text{CN})_2 \cdot 2\text{NH}_3$.—When preparing Fleurent's blue compound (*loc. cit.*), if the mixture be heated to 160–170° instead of 140–145°, a white substance is obtained of the above formula; it decomposes easily on exposure to the air, and in contact with ammonia passes into the violet, green, or blue compounds described above.

A. W. C.

Decompositions of Alkyl Thiocyanates. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, **126**, 838–840).—When methyl thiocyanate is mixed with a solution of bleaching powder, there is little action in the cold, but, on warming, nitrogen and carbonic anhydride are liberated, and methylsulphonic acid is formed. A solution of sodium hypochlorite containing excess of sodium hydroxide acts less readily, and some sulphuric acid is formed in addition to the other products. Ethyl thiocyanate is much less readily attacked, and in this case also some sulphuric acid is formed. With a hot solution of sodium hypochlorite containing an excess of the hydroxide, the ethyl salt yields sodium ethylsulphonate and sodium cyanide, but if the action is allowed to continue after all the hypochlorite has been reduced, any excess of the ethyl thiocyanate is converted into ethyl bisulphide, sodium cyanide, and sodium cyanate. Amyl thiocyanate is only slightly attacked under similar conditions, but the products are analogous.

Methylene thiocyanate, when heated with a concentrated solution of bleaching powder, yields methylenedisulphonic acid, carbonic anhydride, and nitrogen; in presence of excess of alkali, hydrogen cyanide is formed in place of carbonic anhydride and free nitrogen, and traces of cyanic and sulphuric acids are also produced.

Allylic isothiocyanate is but slightly attacked, even in hot solutions; some nitrogen is liberated, and some sulphuric acid is produced.

C. H. B.

Remarks on the Action of Chlorine on Ethylic Alcohol. By ANDRÉ BROCHET (*Bull. Soc. Chim.*, 1897, [iii], 17, 224—228).—The views of Fritsch and other observers are discussed, and the conviction is expressed that the formation of chlorinated acetals is due to secondary reactions, and is not an essential part of the process (see following abstract).
N. L.

Theory of the Action of Chlorine on Ethylic Alcohol. By ANDRÉ BROCHET (*Bull. Soc. Chim.*, 1897, [iii], 17, 228—230).—The chlorination of ethylic alcohol is comparable to that of the higher aliphatic alcohols studied by the author, and is to be explained in a similar manner. It appears that small quantities of ethylic acetate and monochlorethyl alcohol are first formed, but the limit of acidity below which these compounds can exist is soon attained, and from this time dichlorethyl alcohol, $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{OH}$, is constantly produced. The latter, under the dehydrating influence of hydrochloric acid, reacts with alcohol, according to the reaction of Wurtz and Frapollé, and gives rise to dichlorethyl oxide, $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{OEt}$, and, by the further action of chlorine, to trichlorethyl oxide, $\text{CHCl}_2\cdot\text{CHCl}\cdot\text{OEt}$. These compounds react with water to give alcoholates of chlorinated aldehydes, and with alcohol to give chlorinated acetals. The latter are decomposed, as the temperature rises, with re-formation of the chlorinated ethylic oxides, whilst the former are eventually converted into chloral alcoholate by the continued action of chlorine.
N. L.

Combination of Trimethylcarbinol with Mercuric Nitrate. By GEORGES DENIGÈS (*Compt. rend.*, 1898, 126, 1043—1045).—When trimethylcarbinol is boiled with a solution of mercuric nitrate, it yields an insoluble orange compound, which blackens when exposed to light; this explodes when struck or when heated to about 80° , is decomposed by hydrochloric acid, with liberation of unsymmetrical dimethylethylene and formation of mercurous and mercuric chlorides, and by hot solutions of alkali hydroxides with formation of mercurous and mercuric oxides. It does not contain a trimethylcarbinol group, and is to be regarded as a dimethylethylene mercuriosomeric nitrate, $\text{NO}_3\text{Hg}_2\cdot\text{C}_4\text{H}_8\cdot\text{HgNO}_3$.
C. H. B.

Cholesterols from Lower Plants. By ERNEST GÉRARD (*Compt. rend.*, 1898, 909—911).—The cholesterol obtained from cultures of *Staphylococcus alba* in peptonised beef broth differs from the cholesterols obtained from animals or higher plants. With concentrated sulphuric acid, it gives a blood-red coloration, which is not imparted to chloroform when the latter is shaken with the acid; if the sulphuric acid solution is diluted with water, it yields a greenish, and not a white,

precipitate; when a solution in carbon tetrachloride is agitated with concentrated sulphuric acid, the acid becomes blood-red, and the tetrachloride becomes green; if exposed to the air, it alters and becomes coloured.

The cholesterol from *Fucus crispus* behaves in the same way.

It follows that the cholesterols of microbes or of algæ belong to the group of ergosterols, and resemble the cholesterols obtained from cryptogams, but not those obtained from animals or the higher plants.

C. H. B.

Propionaldol. By AUGUST THALBERG (*Monatsh.*, 1898, 14, 154—160).—*Propionaldol*, $C_6H_{12}O_2$, is formed when propaldehyde is allowed to remain in contact with a saturated solution of potassium carbonate, the whole being kept cool. It is a very viscid transparent liquid, which boils at $94-96^\circ$ under a pressure of 23 mm. By reduction with aluminium amalgam, it is converted into the corresponding *glycol*, $CH_2Me \cdot CH(OH) \cdot CHMe \cdot CH_2 \cdot OH$, boiling at 214° , and readily yields an *oxime*, $C_6H_{12}O \cdot NOH$; this is a thick, yellow liquid, which boils at 140° under a pressure of 22 mm. On gentle oxidation, the aldol yields propionic acid and a *hydroxyhexoic acid*, $CH_2Me \cdot CH(OH) \cdot CHMe \cdot COOH$, which is a syrupy liquid and forms an anhydrous *barium salt*. More vigorous oxidation converts this acid into diethyl ketone.

A. H.

Acid Glycerophosphates. By ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1898, 126, 1215—1218).—The acid glycerophosphates, $[C_3H_5(OH)_2O \cdot PO(OH)O]_2M''$, may be prepared by decomposing the corresponding normal salts with the theoretical quantity of sulphuric acid, or by the double decomposition of the acid barium salt with a soluble sulphate. They are uncrystallisable, vitreous substances, readily soluble in water, from which they are precipitated with difficulty by alcohol. Although the potassium and sodium salts cannot be obtained free from water, the barium, zinc, calcium, magnesium, copper, and strontium salts become anhydrous at 120° . Aqueous solutions of acid glycerophosphates are decomposed on boiling, with formation of the normal salt, phosphoric acid and glycerol being liberated. The normal glycerophosphates of pyridine, aniline, phenylhydrazine, quinine, and cocaine have been prepared by agitating ethereal solutions of these bases with an aqueous solution of an acid glycerophosphate. These compounds will be described hereafter.

N. L.

Action of the Sorbose Bacterium on Polyhydric Alcohols. By GABRIEL BERTRAND (*Compt. rend.*, 1898, 126, 762—765).—The conversion of sorbitol into sorbose, and of mannitol into levulose by the action of the sorbose bacterium, are analogous, since in both cases a ketose is produced by oxidation of a secondary alcoholic group in the original compound. The author has therefore investigated the action of the sorbose bacterium on various polyhydric alcohols. Glycol, xylitol, and dulcitol resist the oxidising action of the bacterium, and do not aid in its development. Glycerol, sorbitol, and mannitol (in which the number of carbon atoms is a multiple of three) favour the development of the bacterium, and are converted into reducing sugars

which contain two atoms of hydrogen less than the original alcohol. Erythritol, arabitol, volemitol, and perseitol belong to this second group, and behave in the same way. There is a well-marked stereochemical difference between the two groups, and it seems that those alcohols only are oxidised by the sorbose bacterium which contain a CH·OH chain arranged in such a manner that there is not a hydrogen atom on the same side as the hydroxyl group that is attacked in the oxidation.

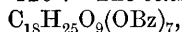
Further investigations are being made.

C. H. B.

Soluble Starch. II. By WIKTOR SYNIEWSKI (*Ber.*, 1898, 31, 1791—1796. Compare this vol., i, 61).—Soluble starch obtained by the author's method has the specific rotatory power $[\alpha]_D = 195.3^\circ$ in a 10 per cent. solution at 20° .

Solutions of higher concentration than 12.5 per cent. become turbid from separation of an insoluble modification, which is formed from soluble starch through elimination of water. Baryta converts soluble starch into the compound $C_{18}H_{32}O_{16}, BaO$.

The *acetyl* derivative, $C_{18}H_{25}O_9(OAc)_7$, is obtained by heating soluble starch with barium carbonate and acetic chloride in sealed tubes at 120° , and afterwards at 140° ; it is a white, amorphous powder, and melts at 110 — 120° . The *benzoyl* derivative,



melts above 120° .

Inversion with hydrochloric acid converts soluble starch into 99.3 per cent. of the amount of dextrose required by the formula $C_{18}H_{32}O_{16}$. Water at 140 — 145° under pressure gives rise to only 3.99 per cent., whilst diastase produces maltose in quantities varying according to the temperature and duration of action.

M. O. F.

Resolution of Starch by the Action of Diastase. By HENRI POTTEVIN (*Compt. rend.*, 1898, 126, 1218—1221).—The explanation of the conversion of starch into dextrin and maltose by a series of hydrolytic decompositions is not in accordance with the experiments of Brown and Heron, who find that the various dextrins are identical as regards composition, molecular weight, and rotatory power. A number of experiments are described which tend to show (1) that the conversion of starch into maltose takes place in two distinct stages. dextrin being the intermediate product; (2) that the difference between the various dextrins is merely one of physical state; (3) that the different parts of the starch granules differ in the ease with which they are converted into dextrin, and the dextrin thus formed into maltose. In consequence of this, when starch is acted on by diastase, the transformation proceeds with unequal rapidity in different portions of the mass, some parts having already been converted into maltose while others are still in the dextrin stage, or, perhaps, not yet attacked.

N. L.

Action of the Silent Electric Discharge on Nitrogenous Carbon Compounds in presence of Free Nitrogen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 126, 775—793).—Experiments were made with many different groups of carbon com-

pounds containing nitrogen. In the case of solid compounds, or liquids having a low vapour pressure, the action could not be pushed to its limit; in almost all cases, nitrogen was absorbed, and condensation products of the nature of polyamines, polyamides, and condensed derivatives were formed. The most notable exceptions to the general rule that nitrogen is absorbed are ethylamine, allylamine, phenylhydrazine, thiocarbamide, ethylenediamine and propylenediamine. Methylamine and nitromethane actually lose nitrogen, probably because in them the ratio of nitrogen to carbon is unity, whereas in the polyamines formed from mononitrogenous compounds it is less than unity. The diamines absorb practically no nitrogen. Compounds of the methane series lose hydrogen at the same time that they combine with nitrogen, the loss being of the same order as in the case of the hydrocarbons and alcohols of the same series. This loss of hydrogen is greatest with the monamines, but not so great with allylamine and ethylene- and propylene-diamines. The cyclic character of the product is more marked the higher the number of carbon atoms in the original compound, but to this general result certain highly oxygenised compounds form exceptions.

Pyrroline, indole, and other aromatic compounds lose no hydrogen when they combine with the nitrogen; pyridine, likewise, loses no hydrogen, but piperidine, on the other hand, loses a relatively large proportion, and tends to change into pyridine.

When the compositions of the polyamines formed from the hydrocarbons, alcohols, and amines are compared, it would seem that, for a given weight of nitrogen, the condensation of the hydrocarbon, for a given number of carbon atoms, increases from the hydrocarbon to the alcohol, and from the latter to the monamine. With diamines, the condensation is double what it is with monamines.

Isomerides, as a rule, behave similarly, but benzylamine and toluidine differ considerably in the amount of nitrogen with which they combine. Methylaniline behaves as if the methyl and phenyl groups acted separately, the two effects being superposed; this cumulative effect is important, and is seen still more distinctly when comparison is made between dimethylamine and ethylamine, trimethylamine, and the propylamines. In the case of amines, the quantity of nitrogen absorbed seems to be proportional to the number of alkylic residues in the amine.

The compounds formed by combination with nitrogen without elimination of hydrogen behave, as a rule, like amines or amides; it is clear that if they are saturated and non-cyclic compounds, they cannot be regarded as direct derivatives of the compound from which they have been formed. In the benzene series, for example, the products must be regarded as derived, not from benzene itself, but from its hydrides.

Albumin combines with a considerable proportion of nitrogen, with liberation of about an equal volume of hydrogen, together with some carbonic anhydride and carbonic oxide, and this result may be of importance in connection with the influence of atmospheric electricity on vital processes.

C. H. B.

Ethylisoamylamines. By AUGUSTE DURAND (*Bull. Soc. Chim.*, 1897, [iii], 17, 405—408).—The pasty mass formed by the action of ethylic iodide on isoamylamine was dissolved in water and distilled with potash, the distillate being received in dilute hydrochloric acid. The secondary base was separated by means of its nitroso-derivative, which was then distilled with steam, and dried with calcium chloride.

Nitrosoethylisoamylamine, $C_5H_{11} \cdot N \cdot Et \cdot NO$, is a thick, golden-yellow liquid, slightly soluble in water, having a persistent, somewhat suffocating odour, and boiling at 144° under a pressure of 85 mm.

Ethylisoamylamine, $C_5H_{11} \cdot NH \cdot Et$, obtained by heating the preceding compound with concentrated hydrochloric acid and subsequently distilling with sodium carbonate, is a thick, colourless liquid of strong ammoniacal odour. It boils at 127° at the ordinary pressure, is slightly soluble in water, and has a sp. gr. = 0.764. The *platinochloride* crystallises in orange-red needles; the *aurochloride* is a syrupy liquid, crystallising with difficulty in small, orange-red needles; and the *oxalate* crystallises in tufts of silky needles.

Diethylisoamylamine, $C_5H_{11} \cdot N \cdot Et_2$, is obtained by distilling with soda the residues from the preparation of ethylisoamylamine, and is identical with the product which Hofmann obtained by the decomposition of triethylisoamylammonium iodide. It is a thick, colourless liquid boiling at 155° (corr.), and having an odour recalling that of pyridine. The *picrate* forms fine yellow crystals melting at 75° .

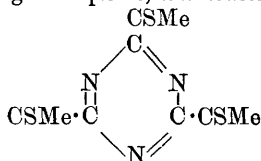
N. L.

Diagnosis of Secondary Aliphatic Amines containing Monatomic Alkyl Groups. By ARMAND BERG (*Bull. Soc. Chim.*, 1897, [iii], 17, 297—300).—It has been shown in a previous note that secondary chloramines are decomposed by alcoholic potash with elimination of hydrogen chloride and formation of an ethylenic linking; isobutylchloramine, for example, yields isobutylisobutylideneamine, which, on hydrolysis, is converted into isobutylamine and isobutaldehyde. The case of an amine containing two different radicles has now been studied.

Ethylisoamylchloramine, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot NCl \cdot Et$, obtained by the action of sodium hypochlorite on ethylisoamylamine hydrochloride, is a yellowish, oily liquid of disagreeable odour, insoluble in water, boiling at 72° under 37 mm. pressure, and of sp. gr. 0.919 at 0° . When treated with rather more than the theoretical quantity of sodium dissolved in alcohol and finally mixed with water, an oily liquid separates which cannot be distilled without decomposition. On distillation with a slight excess of hydrochloric acid, a mixture of valeraldehyde and acetaldehyde passes over, whilst the residue, when distilled with potash, yields ethylamine and isoamylamine. It appears, therefore, that the decomposition of ethylisoamylchloramine takes place in both of the ways theoretically possible, with formation of isoamylethylideneamine, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot N : CHMe$, or ethylisoamylideneamine, $CHMe_2 \cdot CH_2 \cdot CH : N \cdot Et$. On hydrolysis, the former yields isoamylamine and acetaldehyde, whilst the latter yields ethylamine and valeraldehyde. The constitution of the original base is thus clearly shown by the products obtained by the successive action of alcoholic potash and of acids.

N. L.

Derivatives of Symmetrical Triazine. By JULIUS TROEGER and V. HORNING (*J. pr. Chem.*, 1898, [ii], 57, 357—365).—Attempts to replace the chlorine atoms in solid α -dichlorocyanethine (hexachlorotriethylcyanidine) without breaking the triazine ring, by acting on it with moist silver oxide, silver carbonate, potassium acetate, or alcoholic potash, proved unsuccessful; but when it is treated with alcoholic potassium hydrogen sulphide, *trithioacetylcyandine*



is obtained as a white, amorphous substance. It burns with great difficulty when heated on platinum foil, and is entirely decomposed on heating with concentrated acids.

Acetyldithioacetylcyandine, $\text{C}_3\text{N}_3\text{Ac}(\text{CSMe})_2$, produced by the action of alcoholic potassium sulphide on dichlorocyanethine, is an ochre-brown, amorphous substance possessing no melting point.

The great insolubility of both these sulphur compounds in all ordinary reagents renders their purification a matter of extreme difficulty; the only proof of their purity is afforded by the analytical numbers, for no evidence could be obtained from a study of their decomposition products.

A. W. C.

Action of the Silent Electric Discharge on Aldehydes and Nitrogen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 126, 671—680).—The author continues his researches on the action of the silent electric discharge on mixtures of nitrogen with various carbon compounds, and in this paper describes the results of experiments with various compounds having an aldehydic function; acetaldehyde, propaldehyde, acetone, dimethylmethylal, aldol, paraldehyde, trioxymethylene, camphor, benzaldehyde, benzoin, cinnamaldehyde, salicylaldehyde, furfuraldehyde, quinone, glucose, cellulose, and humus. In all cases there is absorption of nitrogen, accompanied by liberation of hydrogen, the volume of which, however, is always considerably smaller than the volume of the nitrogen absorbed, and in the case of the polymerides of aldehyde, and of aldehydes of the benzene and campholic series, is very small indeed. The quantity of nitrogen absorbed is comparatively high in the case of primary aldehydes, ketones, quinone, camphor, and furfuraldehyde and compounds similar to dimethylmethylal, but is low in the case of the polymerides of aldehyde, benzoin, glucose, cellulose and its derivatives. With solids and the less volatile liquids, it is very difficult to obtain the maximum possible amount of change, owing to the low vapour pressures of the compounds.

The products are condensed compounds of the nature of amides or amines, and belong to the same class as the ammoniacal compounds of the aldehydes; they resemble more especially the glycosines, glyoxalines, and polyamines containing a low proportion of hydrogen.

Aldehyde absorbs less nitrogen than propaldehyde, and in this

reaction seems to behave like a methane derivative rather than like the higher homologues. Propaldehyde and acetone absorb practically the same proportion of nitrogen. The influence of polymerisation is uncertain, owing to the difficulty of reaching the limit of the reaction in the case of the polymerides.

In the case of isomerides such as propaldehyde and allylic alcohol, the former combines with more than twice as much nitrogen as the latter, whereas ethereal salts of dihydric alcohols combine with more nitrogen than the aldehydes with which they are respectively isomeric. The relative behaviour of isomeric aldehydes and acids, such as salicylaldehyde and benzoic acid, remains uncertain, because the limit of the reaction is very difficult to reach.

Acetaldehyde combines with rather less than one atom of nitrogen; propaldehyde and acetone with nearly three atoms; dimethylmethylal combines with an atom of nitrogen for each atom of carbon. In the case of the other compounds, the results are less definite, but the proportion of nitrogen absorbed is, as a rule, lower the more condensed the original molecule.

C. H. B.

Commercial Preparation of Chloral. By AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1897, [iii], 17, 230—234).—The process is divided into three stages:—1. *Preparation of chloral alcoholate*.—Dry chlorine is passed into absolute alcohol contained in a large glass balloon connected by tubes with one or more vessels of water for absorption of the hydrogen chloride evolved. The temperature is at first kept low, but is afterwards, as the action becomes less violent, gradually raised to 100°. At the end of 10—14 days, the liquid is found to be completely soluble in water; the current of chlorine is then stopped, and, on cooling, a white, solid mass of chloral alcoholate is obtained. The action of the chlorine is facilitated by the addition of iodine (1 per cent.) to the alcohol, or by a little crystallised ferric chloride. 2. *Conversion of chloral alcoholate into chloral*.—The still liquid chloral alcoholate is transferred to an enamelled vessel and gradually mixed with an equal volume of concentrated sulphuric acid, the solution being then heated in a reflux apparatus until hydrogen chloride is no longer evolved. The mixture is then distilled until a temperature of 100° is reached, and the distillate is redistilled, the portion passing over below 94° constituting pure chloral. 3. *Conversion of chloral into chloral hydrate*.—The chloral is mixed with the theoretical quantity of water and the liquid run on to a smooth level surface to cool and solidify, or, if a purer product is required, the still liquid hydrate is mixed with about one-third of its volume of chloroform and allowed to crystallise in closed vessels. After about a week, the crystals are drained, and dried at the ordinary temperature. Benzene or carbon bisulphide may be used instead of chloroform.

N. L.

Acetals of Acetaldehyde and of Glyceraldehyde. By ALFRED WOHL (*Ber.*, 1898, 31, 1796—1801).—An acetal of acetaldehyde has not yet been prepared, addition of alcohol occurring simultaneously

with acetal formation when the aldehyde is treated with alcohol; the substance can be obtained, however, by an indirect method.

Chloropropionaldehydediethylacetal, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, is prepared by slowly adding acraldehyde to ice-cold, absolute alcohol saturated with hydrogen chloride; it was first obtained by Alsberg (*Jahresbericht*, 1864, 495) on saturating with hydrogen chloride a mixture of acraldehyde and alcohol.

Acraldehydeacetal, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{OEt})_2$, which is formed on heating an intimate mixture of the foregoing substance with caustic potash, occurs in the fraction of the product which boils at $120\text{--}130^\circ$. It is a limpid oil, having a peculiar odour which is not unpleasant, and boils at 123.5° under a pressure of 762 mm.; its sp. gr. = 0.85425 at 15° . Cold dilute hydrochloric acid sets free acraldehyde from the acetal, and bromine gives rise to the dibromide (compare Claisen, this vol., i, 421).

Hydroxychloropropionacetal, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OEt})_2$, is produced by the action of hypochlorous acid on acraldehydeacetal; it is a colourless, somewhat viscous oil, and boils at 126° under a pressure of 32 mm.

Epihydrinaldehydeacetal, $\text{CH}(\text{OEt})_2\cdot\text{CH}\begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{O} \end{smallmatrix}$, is obtained by heating the foregoing substance with potash under reduced pressure; it boils at 165° .

Glyceraldehydeacetal, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OEt})_2$, prepared from hydroxychloropropionacetal either by the action of aqueous potassium carbonate or by direct oxidation with potassium permanganate, is a colourless, viscous liquid, miscible with water and with alcohol, and having a burning taste. It boils at 130° under a pressure of 20.7 mm. Dilute mineral acids hydrolyse the substance very readily, giving rise to glyceraldehyde.

M. O. F.

Product of the Oxidation of Glycerol by the Sorbose Bacterium. By GABRIEL BERTRAND (*Compt. rend.*, 1898, 126, 842—844).—When the sorbose bacterium is allowed to grow in a solution of yeast containing 2 to 5 per cent. of glycerol, the latter is partially converted into dihydroxyacetone, identical with that obtained synthetically by Piloty (this vol., i, 117). It follows that the sorbose bacterium acts on glycerol in the same way as on sorbitol and mannitol, removing H_2 and forming a true ketose.

C. H. B.

Biochemical Production of Dihydroxyacetone. By GABRIEL BERTRAND (*Compt. rend.*, 1898, 126, 984—986).—Dihydroxyacetone is readily produced by the growth of the sorbose bacterium in broth containing 5 to 6 per cent. of glycerol. After removal of the gelatinous bacteroidal membrane, the liquid is distilled in a vacuum at the lowest possible temperature, and the residual syrup is mixed with five or six times its weight of absolute alcohol and two volumes of ether. The ether alcohol solution is drawn off and distilled at a low temperature under diminished pressure, when the residual liquor crystallises; after purification by washing with absolute alcohol, the dihydroxy-

acetone forms small hexagonal lamellæ. With sodium hydrogen sulphite, it forms a crystalline compound, from which it can again be separated in the usual way.

The yield of dihydroxyacetone under favourable conditions may amount to 30 per cent. of the weight of the glycerol taken.

C. H. B.

Action of Alkalis on Citral. Preparation of Methylheptenone. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1897, [iii], 17, 175—193).—When citral is boiled for 12 hours with a solution of potassium carbonate in a reflux apparatus, it is quantitatively converted into acetaldehyde and methylheptenone. The latter boils at 168°, has a sp. gr. = 0·910 at 14°, and a refractive index $n_D = 1·437$ at 31°; it is identical with the methylheptenone obtained by other experimenters and synthesised by Barbier and Bouveault. Admitting the formula, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, proposed by these observers for methylheptenone, it follows that citral is 2 : 6-dimethyl-2 : 6-octadiene-8-al, $\text{CH}_3\cdot\text{CMe}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\text{:CH}\cdot\text{COH}$. The crude citral extracted from essence of lemon-grass by means of sodium hydrogen sulphite is a mixture of 90 per cent. of citral with 10 per cent. of methylheptenone. The latter may be separated by fractional distillation under diminished pressure, but complete purification is only to be effected by converting it into the oxime which has already been described; as prepared by the author, it boils at 120° under 25 mm. pressure, has a sp. gr. = 0·919 at 14°, and a refractive index $n_D = 1·475$ at 29°.

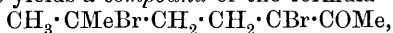
When methylheptenone and phenylhydrazine are mixed in molecular proportion, a *hydrazone* is produced, from which methylheptenone may be regenerated by the action of acids. If, however, the hydrazone be heated to about 130°, isomeric change takes place accompanied by a rise in temperature, and, on distillation, a yellowish oil, of sp. gr. = 0·985 at 0°, is obtained, which dissolves in acids without decomposition. This *compound* is also obtained by the action of phenylhydrazine on 2-methyl-6-heptanone-3-ol (see below), and must therefore be represented by the formula $\text{CMe}_2\text{:CH}\text{:CH} < \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{NPh} \text{---} \text{N} \end{smallmatrix} > \text{CMe}$. When

methylheptenone is shaken with hydrochloric acid, 2-methyl-2-chloro-6-heptanone, $\text{CH}_3\cdot\text{CClMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, is formed, and the corresponding *bromine* and *iodine* derivatives are obtained by the action of hydrobromic and hydriodic acids. They are unstable liquids of pleasant, fruity odour, and are more easily prepared from trimethyldihydrohexone (see below), a cyclic isomeride of methylheptenone.

The main product of the action of concentrated sulphuric acid (75 per cent.) on methylheptenone is dihydrometaxylene [$\text{Me}\text{:Me}\text{:H}\text{:H} = 1 : 3 : 5 : 6$], previously obtained by Wallach by the action of zinc chloride on methylheptenone; it was identified by its physical properties and by its conversion into dinitrometaxylene. The action of chromyl chloride, in carbon bisulphide solution, on dihydrometaxylene was investigated. The principal product of the reaction is an unstable *chlorine* derivative, $\text{C}_8\text{H}_{11}\text{Cl}$, but metatolualdehyde is also formed.

With less concentrated sulphuric acid (40—50 per cent.), methylheptenone yields a tertiary alcohol, 2-methyl-6-heptanone-2-ol, and a secondary alcohol, 2-methyl-6-heptanone-3-ol, both having the empirical formula $C_8H_{16}O_2$.

2-Methyl-6-heptanone-2-ol, $CH_3 \cdot CMe(OH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COMe$, may be obtained in crystals melting at 68° , but usually exists as an oily liquid having an odour of camphor, and boiling at 124° under 23 mm. pressure. With the halogen acids, it yields 2-chloro-, 2-bromo-, and 2-iodo-2-methyl-6-heptanone. The *hydrazone* is a thick, yellowish liquid boiling at 226° under 28 mm. pressure, and the *oxime* is a viscous syrup boiling at 172° under 32 mm. pressure. When distilled under the ordinary pressure, 2-methyl-6-heptanone-2-ol loses water and is converted into *trimethyldihydrohexone*, $CH_2 \begin{smallmatrix} < CH_2 \cdot CMe_2 \\ CH = CMe \end{smallmatrix} > O$, isomeric with methylheptenone. It is a liquid of ethereal odour boiling at 129° , having a sp. gr. = 0.883 at 14° , and a refractive index $n_D = 1.470$ at 23° . When boiled for some time with water, it is converted into 2-methyl-6-heptanone-2-ol, whilst it dissolves in dilute sulphuric acid, giving a solution from which alkalis liberate the same compound. The halogen acids give rise to the same derivatives as are obtained from methylheptenone (see above). Bromine dissolved in methylic bromide yields a *compound* of the formula



and having an extremely irritating odour, whilst with hydroxylamine the viscous oxime of 2-methyl-6-heptanone-2-ol is produced. On oxidation with potassium permanganate, trimethyldihydrohexone yields levulinic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$, and, probably, also acetone.

2-Methyl-6-heptanone-3-ol, $CH_3 \cdot CHMe \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot COMe$, boils at 127° under a pressure of 27 mm.; its sp. gr. is 0.950, and its refractive index $n_D = 1.456$ at 23° . With phenylhydrazine, it yields a compound identical with that obtained from methylheptenone, whilst heating with zinc chloride under reduced pressure converts 2-methyl-6-heptanone-3-ol into methylheptenone and dihydrometaxylene.

Synthesis of Methylheptenone.—Acetylpropylic alcohol, obtained by boiling with hydrochloric acid the product of the action of ethylenic bromide on ethylic sodacetoacetate, is treated with fuming hydriodic acid. The *iodide*, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2I$, thus obtained, having a sp. gr. = 1.391 at 0° , and boiling at 109 — 110° under 25 mm. pressure, is left in contact with excess of acetone and finely divided zinc for three months. The *tertiary alcohol*, $CMe_2(OH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COMe$, produced in this reaction yields, on dry distillation, a small quantity of trimethyldihydrohexone which is then converted, by successive treatment with hydriodic acid and caustic soda, into 2-methyl-2-heptene-6-one.

N. L.

Action of the Silent Electric Discharge on Organic Acids and Nitrogen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 126, 681—691).—Experiments were made with acetic, propionic, and formic acids, methylic formate, ethylic formate, and methylic acetate, crotonic, benzoic, succinic, maleic, fumaric, orthophthalic, camphoric,

glycollic, lactic, malic, tartaric, hydroxybenzoic, pyruvic, levulinic, and dehydracetic acids and ethylic acetoacetate.

As a rule, the acids combine with nitrogen under the influence of the discharge; two molecules of acetic or propionic acid combine with three atoms of nitrogen; in other cases, the limit of the reaction was not reached, owing to the low vapour pressure of the acid. As a rule, hydrogen was liberated either in very small quantity or not at all, and in this respect the acids differ from the aldehydes. The liberation or non-liberation of hydrogen seems to be connected with the quantity and function of the oxygen contained in the compound; it is less with aldehydes than with alcohols, and much less with acids than with aldehydes. As a rule, there is little or no formation of carbonic oxide or carbonic anhydride, and therefore the whole of the oxygen remains in the compound formed; maleic and pyruvic acids are, however, exceptions, and yield carbonic oxide, whilst glycollic acid yields carbonic anhydride. Formic acid also yields carbonic oxide and carbonic anhydride, but in other ways also it behaves differently from other acids of the same series, probably because it is decomposed by the discharge; only a very small quantity of nitrogenous product is formed, and this is due to a secondary reaction. The alkylic formates absorb a considerable quantity of nitrogen, and yield both carbonic oxide and carbonic anhydride, due probably to the fact that the acidic and alkylic groups each react in their own special way with the nitrogen under the influence of the discharge. Analogous phenomena are observed when the behaviour of the alkylic formates is compared with that of their isomerides, such as propionic acid. The existence of two groups of reactions, which take place almost independently, is a specially noteworthy point.

Another remarkable result is the great difference in the behaviour of maleic and fumaric acids; the latter absorbs no nitrogen, and liberates neither carbonic anhydride nor carbonic oxide, whereas the former absorbs a considerable quantity of nitrogen and liberates a considerable quantity of carbonic oxide, mixed with some carbonic anhydride.

The rate at which the various monobasic and dibasic acids, whether of simple or complex function, absorb nitrogen, varies considerably, and depends on the constitution and physical condition of the particular acid. Fumaric acid is quite exceptional in absorbing no nitrogen at all.

Olive oil absorbs traces of nitrogen only, but is converted into a peculiar, white, gelatinous polymeride, insoluble in ether or alcohol.

C. H. B.

Hydrated Sodium Formate. By ALBERT COLSON (*Bull. Soc. Chim.*, 1897, [iii], 17, 165).—If, in Berthelot's synthesis of sodium formate, the temperature be about 20°, the anhydrous salt is produced, whereas at 0°, long, orthorhombic needles are formed having the composition $C_2HNaO_2 + 4H_2O$.

N. L.

Solid Acetic Peroxide. By ALBERT COLSON (*Bull. Soc. Chim.*, 1897, [iii], 17, 165).—On evaporating an ethereal solution of acetic peroxide in a vacuum, it is obtained in hard crystals melting at 27° and slowly subliming at the ordinary temperature without melting. It detonates with violence when warmed.

N. L.

Solidifying Points of Pure Stearic and Palmitic Acids, and of their Mixtures. By L. E. O. DE VISSER (*Rec. Trav. Chim.*, 1898, 17, 182—189. Compare Heintz, *Ann. Phys. Chem.*, 92, 588).—The solidifying point of stearic acid is $69\cdot32^{\circ}$, or $69\cdot247^{\circ}$ on the scale of the hydrogen thermometer, and of palmitic acid $62\cdot618^{\circ}$, or $62\cdot532^{\circ}$ on the hydrogen thermometer. The following table gives the solidifying points of mixtures of the two.

Per cent. stearic acid.	Solidifying point.	Per cent. stearic acid.	Solidifying point.	Per cent. stearic acid.	Solidifying point.
100	$69\cdot32^{\circ}$	48	$56\cdot40^{\circ}$	37	$55\cdot75^{\circ}$
90	$67\cdot02$	47	$56\cdot40$	36	$55\cdot62$
80	$64\cdot51$	46	$56\cdot39$	34	$55\cdot38$
70	$61\cdot73$	45	$56\cdot38$	32	$55\cdot12$
60	$58\cdot76$	44	$56\cdot36$	30	$54\cdot85$
55	$57\cdot20$	43	$56\cdot31$	29	$54\cdot92$
54	$56\cdot85$	42	$56\cdot25$	25	$55\cdot46$
53	$56\cdot63$	41	$56\cdot19$	20	$56\cdot53$
52	$56\cdot50$	40	$56\cdot11$	15	$57\cdot80$
51	$56\cdot44$	39	$56\cdot00$	10	$59\cdot31$
50	$56\cdot42$	38	$55\cdot88$	0	$62\cdot618$
49	$56\cdot41$				

These numbers differ somewhat from those obtained by Heintz, but the latter are undoubtedly incorrect, as the capillary tube method was employed.

The results have been mapped out in the form of a curve which exhibits two breaks, one corresponding with a mixture containing 54 per cent. of stearic acid, and the other with a mixture containing 47·5 per cent. of stearic acid. This second break indicates that when a mixture containing 47·5 per cent. of stearic acid solidifies, both solid and liquid portions have the same composition.

J. J. S.

Unsymmetrical Dimethylsuccinic Acid and its Alkyl Salts. By EDMOND E. BLAISE (*Compt. rend.*, 1896, 126, 753—755).—Unsymmetrical dimethylsuccinic acid is obtained by the action of ethylic sodiomalonate on ethylic bromisobutyrate, hydrolysis of the resulting alkyl salt, and decomposition by heat of the tricarboxylic acid thus produced. Some α -methylglutaric acid is formed at the same time, but the production of this acid is minimised by using xylene as the solvent instead of alcohol.

The dimethylsuccinic acid was mixed with ten times its volume of absolute alcohol containing 1 per cent. of hydrochloric acid, and the mixture heated for some time in a reflux apparatus; the product was titrated with a solution of sodium ethoxide, the alcohol distilled off, and the residue diluted with water and agitated with light petroleum. The latter removes the normal salt, which can be obtained by evaporation, after drying the solution over anhydrous sodium sulphate. The results, as compared with those given by succinic acid under the same conditions, are as follows.

	Duration of reaction.	Alkyl salt.		Free acid.
		Normal.	Acid.	
Succinic acid	10 hours	6.36	1.57	—
	20 „	6.59	0.99	—
	30 „	6.86	0.54	—
Dimethylsuccinic acid	10 „	0.49	0.34	1.82
	20 „	1.27	3.68	0.98
	30 „	2.19	3.23	0.68

With dimethylsuccinic acid, as with succinic acid, the two carboxyls are not alkylised simultaneously, and it would seem that the acid function of the one is increased by the presence of the other, so that, as one becomes alkylised, the other becomes less and less readily attacked. Where the acid is unsymmetrical, the energies of the two functions are very different, the tertiary carboxyl being much less readily alkylised than the primary carboxyl. On the other hand, the limit of alkylisation seems to be practically identical in the two cases. There seems to be no constant relation between the proportions of normal and acid alkyl salts formed at various stages of the reaction.

The different rates of formation of normal and acid salts make it comparatively easy to ascertain whether a substituted succinic acid is symmetrical or unsymmetrical. On the other hand, the two acid functions of dimethylsuccinic acid show no differences of the same order as those observed by Friedel in the case of camphoric acid.

C. H. B.

New Synthesis of $\beta\beta$ -Dimethylglutaric Acid. By EDMOND E. BLAISE (*Compt. rend.*, 1898, 126, 1153—1155).—According to Fichter and Herbrand (*Abstr.*, 1896, i, 643) methylsuccinic anhydride, when

reduced with sodium amalgam, yields a lactone, $\begin{array}{c} \text{CHMe}\cdot\text{CO} \\ | \qquad \diagup \text{O} \\ \text{CH}_2-\text{CH}_2 \end{array}$; but it is now shown that unsymmetrical dimethylsuccinic anhydride, when reduced in a similar manner, yields $\begin{array}{c} \text{CMe}_2\cdot\text{CH}_2 \\ | \qquad \diagup \text{O} \\ \text{CH}_2-\text{CO} \end{array}$, a colourless liquid

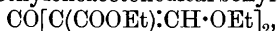
boiling at 207—210°. This liquid is heated with finely divided potassium cyanide for 5 hours at 275—280° in sealed tubes, the product is dissolved in water, and after the unaltered lactone has been extracted with ether, the boiling aqueous solution is saturated with hydrogen chloride, evaporated to dryness, and the residue extracted several times with ether; the ethereal solution deposits $\beta\beta$ -dimethylglutamic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CONH}_2$, in crystalline needles melting at 146°. This amic acid is not hydrolysed when boiled with concentrated hydrochloric acid, but when heated with alkalis yields $\beta\beta$ -dimethylglutaric acid (Perkin and Goodwin, *Trans.*, 1894, 64, and Auwers, *Abstr.*, 1895, i, 410).

J. J. S.

Action of Dilute and Concentrated Alkalis on d -Tartaric Acid. By J. BOESEKEN (*Rec. Trav. Chim.*, 1898, 17, 224—230).—Holleman has shown (this vol., i, 515) that concentrated sodium hydroxide converts d -tartaric acid into racemic and mesotartaric acids. The author now shows that less concentrated alkali yields mesotartaric

acid. Racemic acid can be formed, not only directly from *d*-tartaric acid, but also from mesotartaric acid; this transformation is, however, reciprocal, since racemic acid, when boiled with sodium hydroxide, is partially converted into mesotartaric acid. J. J. S.

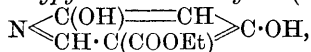
Condensation of Ethylic Acetonedicarboxylate with Ethylic Orthoformate. By GIORGIO ERRERA (*Ber.*, 1898, 31, 1682—1692).—It has been shown by Claisen that the action of ethylic orthoformate on ethereal salts of β -ketonic acids proceeds in one of two directions, according as acetic chloride or acetic anhydride is employed as the condensing agent, and the first of these changes has been studied in the case of ethylic acetonedicarboxylate (*Abstr.*, 1896, i, 463). The author finds that when the latter substance combines with ethylic orthoformate under the influence of acetic anhydride, ethylic ethoxymethyleneacetonedicarboxylate, $\text{OEt}\cdot\text{CH}:\text{C}(\text{COOEt})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt}$, and ethylic diethoxymethyleneacetonedicarboxylate,



are produced; these compounds have not been actually isolated, but their existence is indicated by the nature of the products formed by the action of ammonia. Furthermore, the two ethereal salts interact in molecular proportion, yielding ethylic methenyl-bisacetonedicarboxylate, $\text{COOEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}(\text{COOEt})\cdot\text{CH}:\text{CH}(\text{COOEt})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt}$, which undergoes internal condensation, forming ethylic hydroxytrimesate.

Ethylic hydroxytrimesate, $\text{CH}\begin{smallmatrix} \text{C}(\text{COOEt})\cdot\text{C}(\text{OH}) \\ \text{C}(\text{COOEt})\text{---CH} \end{smallmatrix} \text{C}\cdot\text{COOEt}$, is obtained in the following manner. Ethylic acetonedicarboxylate (1 mol.), ethylic orthoformate (1 mol.), and acetic anhydride (2 mols.), are boiled in a reflux apparatus during 1 hour, and the portion which boils above 120° is then treated with concentrated, aqueous ammonia; a considerable proportion of a reddish-yellow precipitate separates during the next few hours, and this product, when dry, yields two substances on recrystallisation from benzene. Ethylic hydroxytrimesate is the more readily soluble, and crystallises from hot alcohol in colourless needles melting at 83° .

Ethylic 2 : 4-dihydroxypyridine-5-carboxylate (dihydroxynicotinate),



the less soluble substance, crystallises from water in lustrous, white needles, and from benzene in leaflets; it melts and decomposes at 213° . The *barium* derivative is crystalline, and contains $6\text{H}_2\text{O}$. The *acetyl* derivative crystallises from alcohol in lustrous, white needles, and melts at $147\text{--}148^\circ$. The *bromo*-derivative, $\text{C}_8\text{H}_5\text{NBrO}_4$, obtained by the action of bromine water, crystallises from alcohol in white needles; it becomes yellow when exposed to light, and blackens at 225° . *2 : 4-Dihydroxypyridine-5-carboxylic (dihydroxynicotinic) acid* is prepared by the action of alkalis on the ethylic salt; it crystallises from water in microscopic needles and melts at 310° . The *bromo*-derivative, $\text{C}_6\text{H}_4\text{NBrO}_4$, separates from alcohol as a crystalline powder; it chars at 250° , but does not melt.

2:4-Dihydroxypyridine, $N \begin{smallmatrix} \text{C(OH) \cdot CH} \\ \text{CH=CH} \end{smallmatrix} \text{C}\cdot\text{OH}$, is obtained from dihydroxynicotinic acid or its ethereal salt by heating it with concentrated hydrochloric acid at 160° for 2 hours, and subsequently at $190\text{--}200^\circ$; it melts and decomposes at $260\text{--}265^\circ$, and separates from alcohol in lustrous, transparent crystals belonging to the rhombic system; $a:b:c=0.6134:1:1.29473$. The base is almost insoluble in ether, and dissolves very sparingly in cold water or alcohol; the aqueous solution is feebly acidic, and develops a reddish-brown coloration with ferric chloride. The dibromo-compound, $C_5H_3NBr_2O_2$, crystallises from water in colourless needles, and chars at $225\text{--}240^\circ$. The ethylic ether (diethoxypyridine), which is prepared by the action of ethylic iodide on the silver derivative, boils at $230\text{--}232^\circ$; it is heavier than water, is very volatile in an atmosphere of steam, and has an intense odour of pyridine. The platinochloride crystallises from alcohol in orange needles, and the mercurichloride in colourless needles melting at 167° . The dibenzoyl derivative of dihydroxypyridine crystallises from dilute alcohol in lustrous leaflets, and melts at 103° .

Ethylic 4-pyridone-3:5-dicarboxylate, $NH \begin{smallmatrix} \text{CH:C(COOEt)} \\ \text{CH:C(COOEt)} \end{smallmatrix} \text{CO}$, is prepared by heating ethylic acetonedicarboxylate (1 mol.), ethylic orthoformate (2 mols.), and acetic anhydride (4 mols.) in a reflux apparatus during 1 hour, and treating the fraction of the product which boils above 140° with alcoholic ammonia. The precipitate is a mixture of ethylic dihydroxynicotinate with the ammonium derivative of ethylic hydroxytrimesate. The mother liquor, on evaporation, yields ethylic pyridonedicarboxylate, which crystallises from alcohol in lustrous needles, and melts at 251° . When heated with concentrated hydrochloric acid at 165° , it yields the acid, which melts and decomposes at 315° ; at a still higher temperature ($210\text{--}215^\circ$), the action of hydrochloric acid gives rise to γ -pyridone. M. O. F.

Some Furfuran Derivatives. By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 419—424).—Attempts were made to prepare furfuranamine, $C_4OH_3\cdot NH_2$; by the action of bromine and potash on pyromucamide; by the decomposition of pyromucic hydrazide; and by the reduction of nitrofurfuran. Of the methods indicated, the last named alone was successful, and the results obtained by it will be subsequently described.

When pyromucamide is treated with bromine, a mixture of bromine additive products appears to be formed, whilst part of the amide suffers complete decomposition. No better results were obtained by the use of a solution of alkali hypobromite containing a very slight excess of bromine. Since Hofmann's reaction appears not to have been applied to aromatic amides, the behaviour of benzamide and cinnamamide was studied. The former, as was found by Linebarger (*Abstr.*, 1894, i, 332), is first converted into benzoylbromamide,



from which, by warming with 30 per cent. sodium hydroxide solution, aniline is readily obtained. Cinnamamide, on the other hand, yields

a red additive product, $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}_2\text{Br}_2$, which is converted by the action of soda into β -bromocinnamylbromamide, $\text{CHPh}\cdot\text{CBr}\cdot\text{CO}\cdot\text{NHBr}$; and this, by further treatment with alkalis, is decomposed, with liberation of ammonia. β -Bromocinnamylbromamide crystallises, when pure, in colourless needles melting at 188° .

When heated for some hours with hydrazine hydrate, ethylic pyromucate is converted into *pyromucic hydrazide*, $\text{C}_4\text{OH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, which forms colourless scales melting at 30° and soluble in water and alcohol. *Pyromucazide*, $\text{C}_4\text{OH}_3\cdot\text{CO}\cdot\text{N}_3$, obtained by the action of sodium nitrite in acetic acid solution on the hydrazide, crystallises from chloroform in scales melting at 90° , and detonating when heated a little above that temperature. When heated with ethylic alcohol, it is quantitatively converted into the *urethane*, $\text{C}_4\text{OH}_3\cdot\text{NH}\cdot\text{COOEt}$, which could not be crystallised; the corresponding *methylic* derivative forms small prisms melting at 135° . The urethane was completely decomposed by hydrochloric acid, and, on heating with ammonia, only a few drops of a basic liquid, boiling at about 150° , were obtained; a quantity insufficient for purification and identification. N. L.

Oxidation of some Amides and Thioamides. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, 126, 907).—Acetamide is not affected by dilute solutions of hypochlorites, but is oxidised by strong solutions, with liberation of nitrogen. The reaction is readily observed with a warm, concentrated solution of bleaching powder.

Thiocarbamide is less readily attacked than carbamide by an alkaline solution of sodium hypochlorite, and the decomposition is represented by the equation $\text{CSN}_2\text{H}_4 + 7\text{O} = \text{CO}_2 + \text{SO}_3 + \text{N}_2 + 2\text{H}_2\text{O}$. Phenylcarbamide is decomposed by the same reagent, especially on heating. Phenylthiocarbamide is much less readily attacked, the reaction in the early stages being $2\text{NH}_2\cdot\text{CS}\cdot\text{NHPh} + 11\text{O} = 2\text{CO}_2 + 2\text{SO}_3 + \text{H}_2\text{O} + \text{N}_2 + 2\text{Ph}\cdot\text{NH}_2$.

Sarcosine is slowly attacked by hot solutions of hypochlorites, whilst ethylic oxamate is decomposed slowly in the cold, and more rapidly on heating, the products being nitrogen, carbonic anhydride, water, and alcohol. C. H. B.

Yield of Carbamide obtained from Ammonium Carbonates. By LÉON BOURGEOIS (*Bull. Soc. Chim.*, 1897, [iii], 17, 474—477).—Ammonium sesquicarbonate coarsely powdered was heated in a sealed tube at about 130° for 6 hours, the tube was then opened to relieve the pressure, and the operation of heating, &c., repeated until there was no longer any evolution of gas on opening the tube. On dissolving the contents of the tube in water and evaporating the solution to dryness, a residue of carbamide was obtained, which, in a series of experiments, ranged from 3.2 to 9.5 per cent. of the weight of ammonium sesquicarbonate employed. Ammonium bicarbonate and ammonium carbamate, when treated in a similar manner, yield respectively 2.5—2.9 and 2.6—3.7 per cent. of carbamide. In one experiment, in which 600 grams of ammonium sesquicarbonate were heated in a steel autoclave, the metal was found to be attacked, with formation of much ferrous carbonate, and 45.3 grams (7.55 per cent.) of carbamide was obtained.

N. L.

Occurrence of Methylpentamethylene in Light Petroleum from the Caucasus. By OSSIAN ASCHAN (*Ber.*, 1898, 31, 1803—1806. Compare Markownikoff, *Abstr.*, 1897, i, 401).—The fraction of Caucasian naphtha which boils at 71° , and has the sp. gr. = 0.7145 at $20^{\circ}/4^{\circ}$, yields succinic and acetic acids, showing that the hydrocarbon oxidised is methylpentamethylene; nearly 7 per cent. of nitrobenzene is also produced. M. O. F.

Application of Ortho-xylylenic Bromide in Characterising Bases. By MAX SCHOLTZ (*Ber.*, 1898, 31, 1707—1709. Compare this vol., i, 383, 471, and 567).—According to their behaviour towards ortho-xylylenic bromide, amines may be divided into the following eight groups.

1. Primary aliphatic amines, which yield xylyleneimines (dihydro-isindoles), $C_6H_4:(CH_2)_2:NR$.

2. Secondary aliphatic amines, forming ammonium bromides of the type $C_6H_4:(CH_2)_2:NBrR_2$.

3. Tertiary aliphatic amines, which combine with a half molecular proportion of xylylenic bromide, yielding diammonium bromides of the type $C_6H_4(CH_2 \cdot NBrR_3)_2$.

4. Primary aromatic amines, having the ortho-positions unoccupied; these behave like primary aliphatic amines, but the products are not basic (this vol., i, 383).

5. Primary aromatic amines with a substituent in the ortho-position; these yield derivatives of xylylenediamine having the constitution $C_6H_4(CH_2 \cdot NHR)_2$.

6. Primary aromatic amines having both ortho-positions occupied do not combine with ortho-xylylenic bromide.

7. Secondary aromatic amines, which give rise to derivatives of xylylenediamine having the constitution $C_6H_4(CH_2 \cdot NR_2)_2$.

8. Tertiary aromatic amines are indifferent towards ortho-xylylenic bromide. M. O. F.

Hexethylbenzene. By PAUL JANNASCH and A. BARTELS (*Ber.*, 1898, 31, 1716—1718).—By a simple method, details of which will be given later, the authors have obtained hexethylbenzene from benzene, ether, and aluminium chloride.

Diamidotetretethylbenzene is obtained by reducing with tin and hydrochloric acid the dinitro-derivative produced by the action of nitric acid on hexethylbenzene in presence of sulphuric acid; it melts at 92° , and forms large, white crystals which become pink, and finally reddish-brown in air. When boiled with ferric chloride, it yields a compound which melts at 56° and has the odour of quinene. M. O. F.

Attempts to Prepare $\alpha\alpha\beta$ -Triphenylethane. By J. RAWITZER (*Bull. Soc. Chim.*, 1897, [iii], 17, 477—480).—Unsuccessful attempts were made to prepare $\alpha\alpha\beta$ -triphenylethane, $CH_2Ph \cdot CHPh_2$, (1) by the action of benzene, in presence of aluminium chloride, on chloroethylenic chloride, $CH_2Cl \cdot CHCl_2$; (2) by the action of benzene and aluminium chloride on bromodiphenylethane, $CH_2Ph \cdot CHBrPh$; (3) by the action of sodium on a mixture of benzylic chloride and bromo-

diphenylmethane, CHBrPh_2 . Only dibenzyl was obtained by the first method, whilst from the products of the third reaction diphenylmethane, stilbene, tetraphenylethylene, and tetraphenylethane were isolated. As regards the second method, considerable difficulty was met with in the preparation of bromodiphenylethane, which Marquardt obtained by the action of bromine on diphenylethane. The sole product of this reaction at high temperatures appears to be solid dibromodiphenylethane, whilst the liquid product, presumably containing bromodiphenylethane, obtained at a low temperature, is of variable composition, and decomposes on distillation, with formation of dibenzyl, stilbene, and paradibromobenzyl. It yielded only dibenzyl when treated with benzene in presence of aluminium chloride.

N. L.

Action of Oxidising Agents on Nitrogen Compounds. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, 126, 1042—1043).—The author has continued his observations on the action of hypochlorites on amines and other nitrogen compounds. Hydroxylamine is immediately decomposed; methylamine hydrochloride decomposes slowly in the cold, and rapidly when gently heated; ethylamine hydrochloride is decomposed only when heated; aldehyde ammonia, when heated, yields methane and aldehydine, with a small quantity of nitrogen; aldoxime is readily decomposed in the cold; ethylenediamine, diethylenediamine, and propylenediamine are slightly decomposed, with liberation of nitrogen; the phenylenediamines are partially decomposed, the para-derivative being distinctly the most stable; guanidine is rapidly decomposed, and this is true also of hydrazine hydrochloride, phenylhydrazine, and phenylmethylhydrazine. Cyanuric acid also is rapidly decomposed. Piperidine, nicotine, sparteine, cocaine, ecgonine, and benzoylecgonine are not affected, but antipyrine yields a small quantity of nitrogen.

C. H. B.

Combination of Organic Bases with Metallic Salts. By D. TOMBECK (*Compt. rend.*, 1898, 126, 967—970. Compare Abstr., 1897, 463, 560).—Aniline combines with cadmium, magnesium, zinc, and cupric sulphates to form compounds of the type $\text{M}''\text{SO}_4 \cdot 2\text{NH}_2\text{Ph}$, which form small crystals, and decompose when heated. Nickel sulphate forms the compound $\text{MSO}_4 \cdot 6\text{NH}_2\text{Ph}$, and cobalt sulphate a compound, $\text{CoSO}_4 \cdot 4\text{NH}_2\text{Ph}$.

Cadmium, zinc, and magnesium nitrates form crystalline compounds of the same type, and the acetates seem to behave similarly.

Orthotoluidine and paratoluidine likewise form compounds with metallic sulphates, and these will be described later.

C. H. B.

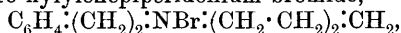
Melting Points and Boiling Points of Aniline, Toluidine, and Xylidine Hydrochlorides. By FRITZ ULLMANN (*Ber.*, 1898, 31, 1698—1700).—The hydrochlorides of aniline, the toluidines, and the xylidines have definite melting points and boiling points, which are collected in the table on the following page.

The salts undergo no change on distillation, which has no influence on the melting point, or on the properties of the free base. It is

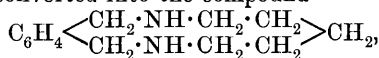
	M. p.	B. p. (728 mm.)	B. p. (760 mm.)
Aniline.....	198°	243°	245°
Orthotoluidine.....	214·5—215	240·2	242·2
Metatoluidine.....	228	247·8	249·8
Paratoluidine.....	243	255·5	257·5
Ortho-xylidine [Me : Me : NH ₂ = 1 : 2 : 3].	254	256	258
Ortho-xylidine [Me : Me : NH ₂ = 1 : 2 : 4].	256	264	266
Meta-xylidine [Me : Me : NH ₂ = 1 : 3 : 4].	235	253·1	255·1
Para-xylidine [Me : Me : NH ₂ = 1 : 2 : 4].	228	245·4	247·4

possible to recognise 2 per cent. of paratoluidine in a specimen of the ortho-base by determining the boiling point of the mixed hydrochlorides; the detection of a small quantity of the para-base has, hitherto, been a matter of some difficulty. M. O. F,

Xylylenediamines : an Undecatonic Ring. By MAX SCHOLTZ (*Ber.*, 1898, 31, 1700—1707. Compare this vol., i, 305, 565).—The author has shown that secondary amines, NHR_2 , combine with ortho-xylylenic bromide, forming substituted ammonium bromides of the type $\text{C}_6\text{H}_4\cdot(\text{CH}_2)_2\cdot\text{NR}_2\text{Br}$, and that these, acting on another molecule of the amine, yield the xylylenediamines, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NR}_2)_2$. It is now found that if ammonia is allowed to act on these ammonium bromides at 200° for 10 hours, bromine is replaced by the amido-group, giving rise to bases of the type $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NHR})_2$. This action may be even applied to xylylenepiperidonium bromide,



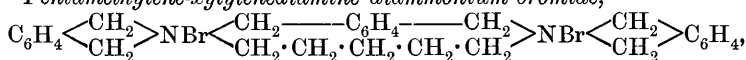
which is thereby converted into the compound



containing eleven atoms in the ring. The production of secondary bases is not, however, without exception: xylylenediethylammonium bromide yields 2'-ethylidihydroisindole, $\text{C}_6\text{H}_4\begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array}\text{NEt}$.

Pentamethylene-xylylenediamine, $\text{C}_6\text{H}_4\begin{array}{c} \text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \end{array}\text{CH}_2$, prepared by heating xylylenepiperidonium bromide with concentrated ammonia at 200° for 10 hours, boils at 180—182° under a pressure of 20 mm. The nitroso-derivative crystallises in transparent needles, and melts and intumesces at 104°. The benzenesulphonamide crystallises from alcohol in colourless prisms, and melts at 132°.

Pentamethylene-xylylenediamine diammonium bromide,



is obtained by heating pentamethylene-xylylenediamine with ortho-xylylene bromide and alcoholic potash; the crystalline substance is hygroscopic, and melts at 65°. The chloride yields a *platinochloride* and an *aurichloride* which crystallise in microscopic needles. The *perbromide* is a yellow, crystalline powder.

Xylylenedi-isobutyl-diamine, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}\cdot\text{C}_4\text{H}_9)_2$, produced on

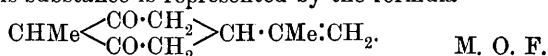
heating xylylene-di-isobutylammonium bromide with ammonia at 200° during 10 hours, is a colourless oil, and boils at 188—190° under a pressure of 20 mm. The *benzenesulphonamide* crystallises in lustrous prisms, and melts at 157°. The *diammonium bromide*, $C_6H_4[CH_2 \cdot N(C_4H_9)Br : (CH_2)_2 : C_6H_4]_2$, forms hygroscopic leaflets melting at 57°.

2'-Ethylidihydroisindole, $C_6H_4 \begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix} NEt$, prepared by heating xylylenediethylammonium bromide with ammonia, boils at 219—220° under atmospheric pressure. The *hydrochloride* is precipitated in needles on adding ether to the alcoholic solution; the *platinochloride* melts at 192°. The *methiodide* melts at 165°, and dissolves very readily in water and alcohol. Ethylidihydroisindole is also obtained by the action of ethylamine on ortho-xylenic bromide. M. O. F.

Oxidation of Hydroxylaminocarvoxime. By CARL D. HARRIES (*Ber.*, 1898, 31, 1810—1812).—Hydroxylaminocarvoxime is prepared by the action of hydroxylamine (2 mols.) on carvone; the *picrate* melts at 150—151°.

Oxidation with mercuric oxide converts it into the *compound* $C_{10}H_{16}N_2O_2$, which melts at 153—155° and has the properties of a dioxime; at the same time, a substance is produced melting at 194° and having the property of reducing Fehling's solution.

When the dioxime is treated with boiling dilute sulphuric acid, hydroxylamine is eliminated, and the *compound* $C_{10}H_{14}O_2$ is formed; this crystallises in lustrous prisms, and melts at 193—194°. The constitution of this substance is represented by the formula



Rearrangement of β -Mesityloxime. By CARL D. HARRIES and RICHARD GLEY (*Ber.*, 1898, 31, 1808. Compare this vol., i, 400).—When the aqueous solution of β -mesityloxime hydrochloride is boiled, it becomes turbid, and subsequently clear; the product is the hydrochloride of diacetonehydroxylamine. M. O. F.

Distinction between Magenta S and Ordinary Magenta, in Schiff's Reaction. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1897, [iii], 17, 196—199).—The author replies to the criticisms of Lefèvre, and maintains that a solution of magenta S (the sodium salt of rosaniline-trisulphonic acid), decolorised by sulphurous acid, has its colour restored on adding pure alcohol, but is not affected by aldehyde unless a large excess of the latter be added. There is, therefore, an essential difference between magenta S and ordinary magenta, in this reaction.

N. L.

Reduction of Colouring Matters of the Type of Rosaniline and Malachite-green. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, [iii], 17, 376—378).—Colouring matters of the type of rosaniline and malachite-green, when completely reduced with zinc dust and acetic acid, are converted into leuco-bases, the colour of which is not restored on exposure to air. If, however, the reduction be effected rapidly and

in the cold, the colour is restored on exposure to air or on boiling, but never attains the intensity of the original tint. This phenomenon is attributed to the fixation of two atoms of hydrogen by each amidogroup, resulting in the formation of colourless derivatives of the type $\text{CCl}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_3$, analogous to those obtained with the mineral acids (Abstr., 1893, i, 332). In the case of basic colouring matters of a different type, such as safranin, methylene-blue, and rhodamine, the original colour is restored in all its intensity by exposing to the air the products of reduction in the cold, the change taking place more quickly if the reduction has been effected by boiling. N. L.

The Supposed Tetrahydrochloride of Leucaniline. A Reply to Miolati. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1897, [iii], 17, 193—196).—The analyses of Miolati are discussed, and the results are shown to be, in reality, more in accordance with the formula of the trihydrochloride, as maintained by the author, than with that of the supposed tetrahydrochloride. N. L.

Azophenols derived from Wroblewski's Bromoparatoluidine [$\text{Br}:\text{Me}:\text{N}_2 = 1:3:6$]. By JOHN THEODORE HEWITT and HENRY E. STEVENSON (*Ber.*, 1898, 31, 1782—1785).—*Bromotolueneazophenol*, [$\text{Br}:\text{Me}:\text{N}_2 = 1:3:6$], crystallises from dilute acetic acid in bright yellow leaflets, and melts at 104° ; it contains $\frac{1}{2}\text{H}_2\text{O}$, and becomes anhydrous at 70° . The *acetyl* and *benzoyl* derivatives melt at 84 — 85° and 137 — 139° respectively; the *benzenesulphonate* crystallises from alcohol in orange leaflets and melts at 115° .

Bromotolueneazo- α -naphthol, [$\text{Br}:\text{Me}:\text{N}_2 = 1:3:6$], separates in red crystals on adding petroleum to its solution in chloroform; it melts at 160° . The *acetyl* and *benzoyl* derivatives melt at 155° and 150° respectively.

Bromotolueneazosalicilic acid, [$\text{Br}:\text{Me}:\text{N}_2 = 1:3:6$], melts at 228° , and the *methyl*ic and *ethyl*ic salts at 134° and 116° respectively.

M. O. F.

Action of Acetaldehyde on Phenylhydrazine. Two Isomeric α - and β -Triethylidenediphenylhydrazones. By HENRI CAUSSE (*Bull. Soc. Chim.*, 1897, [iii], 17, 234—249).—The very variable results obtained by the author, and the indefinite character of the compounds prepared by Fischer, led him to suppose that the reaction between aldehyde and phenylhydrazine is not so simple as at first sight appears, and the whole subject has therefore been reinvestigated, with the following results.

When a solution of aldehyde is gradually added to a solution of phenylhydrazine made alkaline with baryta water, an unstable, crystalline substance melting at 53 — 55° is obtained, which appears to be a molecular combination of phenylhydrazine with another substance (*α -diphenyltriethylidenehydrazone*) melting at 60° .

In acid solution, substances are produced having melting points ranging from 68° to 80° and consisting of mixtures of the two isomeric α - and β -diphenyltriethylidenehydrazones in which the α -, or more fusible, derivative predominates.

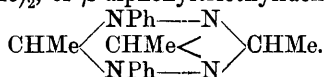
In neutral solutions, on the other hand, a mixture melting at about 90° is obtained, the greater part of which consists of the β -, or less fusible, isomeride.

These substances give the same analytical results, corresponding with the empirical formula $C_{18}H_{22}N_4$, but are distinguished, and separated, from each other by their behaviour towards solvents, the α -compound, of lower melting point, being more soluble in alcohol and less soluble in water than the β -compound.

α -Diphenyltriethylidenehydrazone is best prepared in the pure state by slowly adding aldehyde dissolved in normal phosphoric acid to a solution of phenylhydrazine and sodium thiosulphate. The crystals which separate are washed with small quantities of water and alcohol and recrystallised from the latter. Obtained in this way, α -diphenyltriethylidenehydrazone forms colourless, hygroscopic needles melting at 60° , slightly soluble in cold water but readily dissolved by hot water and by most organic solvents. On exposure to air, it rapidly increases in weight and becomes yellow and red; it is decomposed by mineral acids in the cold and also by acid chlorides; alkalis, however, are without action. With benzaldehyde, it yields colourless needles of *diphenyldibenzylidenehydrazone*, $C_{28}H_{24}N_4$, melting at 156° ; whilst with pyrogallol an unstable crystalline compound, of low melting point, is produced.

β -Diphenyltriethylidenehydrazone is most suitably prepared by gradually adding a solution of aldehyde to a solution of phenylhydrazine phosphate to which some glycerol has been added to moderate the action. A granular deposit is formed from which alcohol dissolves out α -diphenyltriethylidenehydrazone, whilst the residue, when recrystallised from hot alcohol, yields colourless, prismatic crystals of the β -compound melting at 99.5° . The latter is quite stable, remaining unaltered on exposure to air or light; it is insoluble in cold water but slightly soluble in hot water, alcohol, ether, and benzene. It is not affected by concentrated mineral acids in the cold and is only partially decomposed by them on heating, with formation of aldehyde and phenylhydrazine. Alkalis, acid chlorides, benzaldehyde, and pyrogallol are without action on β -diphenyltriethylidenehydrazone.

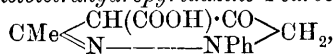
As to the constitution and mode of formation of the compounds described, it is suggested that the interaction of aldehyde and phenylhydrazine first results in the formation of diphenylethylidenedihydrazone, $CHMe(NPh \cdot NH_2)_2$, which is then converted, by the further action of aldehyde, into either α -diphenyltriethylidenehydrazone, $CHMe(NPh \cdot N : CHMe)_2$, or β -diphenyltriethylidenehydrazone,



The latter closed-chain formula is considered to be more in accordance with the great stability of the β -compound. N. L.

Unsymmetrical Phenylhydrazine Derivatives. By HANS RUPE (*Annalen*, 1898, 301, 55—58. Compare Abstr., 1897, i, 409).—Although ethylic chloracetate yields symmetrical derivatives of phenylhydrazine when allowed to act on the base, chloracetamide chloracetanilide, and chloracetyldimethylparaphenylenediamine give rise to unsymmetrical phenylhydrazido-compounds (compare following abstracts). M. O. F.

Unsymmetrical α -Phenylhydrazidoacetanilide. By HANS RUPE and GEORG HEBERLEIN (*Annalen*, 1898, 301, 58—69. Compare Abstr., 1895, i, 521).—The compound obtained from phenylhydrazidacetanilide and ethylic acetoacetate crystallises from alcohol in slender needles, and melts at 147°. Concentrated sulphuric acid converts it into 1:3-phenylmethyl-5-ketotetrahydropyridazine-4-carboxylic acid,

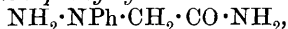


which crystallises in white needles, and melts and decomposes at 230°.

The *acetyl* derivative of phenylhydrazidacetanilide (compare Widman, Abstr., 1893, i, 411) melts at 169·5°.

Diphenyldiketotetrahydrotriazine, $\text{CH}_2 \begin{array}{c} \diagup \text{NPh} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{NPh} \end{array} \text{CO}$, prepared by the action of carbonylic chloride on phenylhydrazidacetanilide dissolved in chloroform, melts at 257—258°; it is insoluble in acids, and dissolves with difficulty in alkalis. M. O. F.

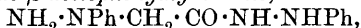
Unsymmetrical Phenylhydrazidacetamide. By HANS RUPE, GEORG HEBERLEIN, and ARMAND ROESLER (*Annalen*, 1898, 301, 69—75).—*Unsymmetrical phenylhydrazidacetamide*,



is obtained by heating chloracetamide with an alcoholic solution of phenylhydrazine (2 mols.); it dissolves readily in alcohol, which allows it to be separated from α -phenylhydrazido- β -acetophenylhydrazine, produced in equal quantity. It melts at 150°, and the *benzylidene* compound at 225°.

Anilidacetamide (*phenylglycinamide*), $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, was first prepared by P. J. Meyer (*C. Soc. J.*, 1876, i, 373); it is most conveniently obtained by heating chloracetamide with alcohol and aniline, and after crystallisation from alcohol melts at 133°. The *nitroso*-derivative forms yellow needles, and melts at 145°; reduction with zinc dust and acetic acid converts it into unsymmetrical phenylhydrazidacetamide (m. p. 150°).

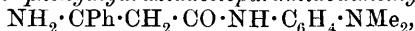
α -Phenylhydrazido- β -acetophenylhydrazine,



is produced in equal quantity with unsymmetrical phenylhydrazidacetamide by the action of chloracetamide on phenylhydrazine; it crystallises from alcohol in lustrous, white leaflets, and melts at 178°. It is also formed when phenylhydrazidacetamide is heated with phenylhydrazine; the *benzylidene* compound melts at 196°. M. O. F.

Unsymmetrical Phenylhydrazidacetoparamidodimethylaniline. By HANS RUPE and JOS. VŠETEČKA (*Annalen*, 1898, 301, 75—79. Compare Abstr., 1897, i, 409).—*Chloracetoparamidodimethylaniline*, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, prepared by the action of chloracetic chloride on paramidodimethylaniline, crystallises from alcohol in slender, white needles, and melts at 146—147°.

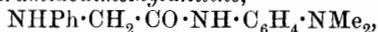
Unsymmetrical phenylhydrazidacetoparamidodimethylaniline,



obtained by the action of the foregoing substance on phenylhydrazine dissolved in alcohol, crystallises in yellow needles or leaflets, and melts at 134—135°. The *benzylidene* compound melts at 184—185°.

and the *acetyl* derivative, which crystallises in nacreous leaflets, melts at 158° ; the *compound* with ethylic acetoacetate melts at 185° .

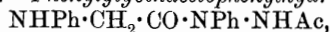
Phenylglycineparamidodimethylaniline,



is produced by the action of chloracetoparamidodimethylaniline on aniline, and melts at 122 — 134° ; the *nitroso*-derivative crystallises in white needles melting at 165° , and does not give Liebermann's reaction. M. O. F.

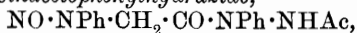
Unsymmetrical α -Phenylhydrazido- α -acetophenylhydrazide.

By HANS RUPE, GEORG HEBERLEIN, and ARMAND ROESLER (*Annalen*, 1898, 301, 79—88).—*Phenylglycinacetophenylhydrazide*,

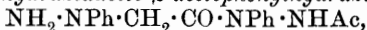


is prepared by the action of aniline on α -chloraceto- β -acetophenylhydrazine, and melts at 141° ; 10 per cent. sulphuric acid hydrolyses it to *phenylglycinephenylhydrazine*, which crystallises from alcohol in white needles and melts at 153 — 154° .

Nitrosophenylglycinacetophenylhydrazide,

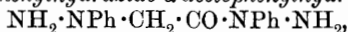


crystallises from alcohol in yellow needles and melts at 98° . *Unsymmetrical phenylhydrazidaceto- β -acetophenylhydrazide*,



obtained by the reduction of the foregoing compound with zinc dust and acetic acid, crystallises from alcohol in cubes melting at 176° ; the *benzylidene* derivative melts at 184° .

Unsymmetrical phenylhydrazido- α -acetophenylhydrazide,

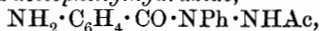


obtained by hydrolysing the *acetyl* derivative with 10 per cent. sulphuric acid, crystallises from dilute alcohol or from benzene in small, white needles melting at 155° ; the *dibenzylidene* and *diacetyl* derivatives melt at 180 — 181° and 198° respectively. The *compound* $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_2$ is produced by the action of carbonylic chloride on phenylhydrazido- α -acetophenylhydrazide; it crystallises from dilute alcohol in small, white needles, and melts at 209 — 210° .

M. O. F.

α -Orthamidobenzophenylhydrazide. By HANS RUPE and ARMAND ROESLER (*Annalen*, 1898, 301, 89—94).— *α -Orthonitrobenzo- β -acetophenylhydrazide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NPh} \cdot \text{NHAc}$, is prepared by heating acetophenylhydrazide dissolved in benzene with orthonitrobenzoic chloride in a reflux apparatus; it crystallises from benzene in white needles, and melts at 134° . According to the reducing agent employed, two different products are obtained from this substance.

α -Orthamidobenzo- α -acetophenylhydrazide,

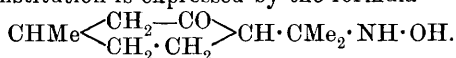


is produced by the action of zinc dust and acetic acid, and crystallises from hot water in large, lustrous crystals melting at 140° ; the *benzylidene* compound forms colourless needles, and melts at 175 — 177° .

α -Orthamidobenzophenylhydrazide, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NPh} \cdot \text{NH}_2$, prepared by reducing the nitro-compound with stannous chloride and hydrochloric acid, also crystallises from water in large, lustrous prisms melting at 134° ; the *platinochloride* forms microscopic, yellow

needles, and is somewhat unstable. The *dibenzylidene* and *diacetyl* derivatives melt at 150—151° and 195—196° respectively. The compound $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NPh} \\ \text{NH} - \text{CO} \end{smallmatrix} \text{NH}$, produced by the action of carbonylic chloride on orthamidobenzophenylhydrazide, crystallises from hot chloroform in slender needles and melts at 218—219°. M. O. F.

Pulegonehydroxylamine. By CARL D. HARRIES and GEORG ROEDER (*Ber.*, 1898, 31, 1809—1810).—Pulegoneoxime hydrate (Beckmann and Pleissner, *Abstr.*, 1891, 936) should be called *pulegonehydroxylamine*, being a cyclic analogue of diacetonehydroxylamine; its constitution is expressed by the formula

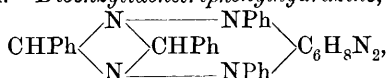


Oxidation converts it into nitrosomenthone and nitromenthone, which melt at 35° and 80° respectively. M. O. F.

Benzylidenediphenylhydrazines and their Derivatives. Transformation into Dibenzylidenediphenyltetrazole. By HENRI CAUSSE (*Bull. Soc. Chim.*, 1897, [iii], 17, 480—485).—Tri-

benzylidenediphenylhydrazine, $\text{CHPh} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{NPh} \\ \text{NPh} \end{smallmatrix} \text{CHPh}$, is pro-

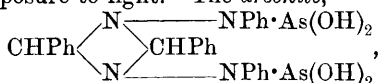
duced by the interaction of benzaldehyde and phenylhydrazine in aqueous or dilute alcoholic solution. It forms colourless, microscopic crystals, insoluble in water, benzene, and chloroform, but slightly soluble in alcohol. *Dibenzylidenetriphenylhydrazine*,



obtained by treating benzaldehyde with phenylhydrazine in presence of alcohol and acetic anhydride, crystallises in colourless, microscopic needles, insoluble in water, somewhat soluble in alcohol. The

antimonite, $\text{CHPh} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{NPh} \\ \text{NPh} \end{smallmatrix} \text{CHPh}$ Sb·OH, obtained by the action

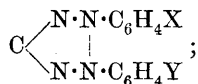
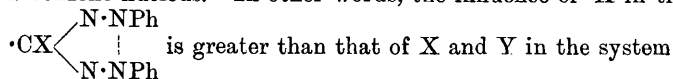
of benzaldehyde on a solution of phenylhydrazine antimonyl tartrate containing excess of antimonious acid, forms colourless needles which become red on exposure to light. The *arsenite*,



is prepared in a similar manner. All the compounds described are decomposed by heat, or by boiling with alcohol, with formation of dibenzylidenediphenyltetrazole melting at 154°. N. L.

Influence of Distance Action exerted by Substituents on the Formation of Tetrazolium Bases. By EDGAR WEDEKIND and LEO STAUWE (*Ber.*, 1898, 31, 1746—1757. Compare this vol., i, 192).—When formazyl derivatives undergo internal condensation and yield tetrazolium bases, substituents attached to the formyl carbon-atom exert a more marked influence than those replacing hydrogen in

a benzene nucleus. In other words, the influence of X in the system

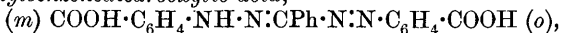


the nitro-group, occupying an ortho-position, is, however, an exception to this generalisation.

The action of the following substituents of formyl hydrogen, arranged in order of increasing influence, has been studied: CN, Ph, COOEt, COPh, N:NPh, COMe, Me, COOH, and H; the yield of tetrazolium base consequently diminishes in the same order, falling from the theoretical amount in the case of cyano-compounds, to 20 per cent. when there has been no replacement of hydrogen.

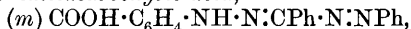
In studying the behaviour of formazyl compounds containing a substituent in one of the benzene groups, the velocity of reaction was so great that it became necessary to study compounds into which a carboxylic group had been already introduced as a retarding agent, compounds of the general formula $\text{C}_6\text{H}_4\text{X}\cdot\text{N:N}\cdot\text{CPh:N:NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$. It was then found that the groups, NO_2 , COOH, COH, COMe, and SO_3H exerted the greatest influence, whilst the substituents, Me, Et, Pr^i , and chlorine displayed unimportant differences in their retarding effect. An orthonitro-group retards more strongly than the same substituent in the meta- and para-positions, which do not differ from one another very considerably in action (compare Bischoff, this vol., i, 131); the influence of ortho-chlorine is unimportant, and the carboxylic groups occupy an intermediate position, in the increasing order, para, meta, and ortho.

Formazylbenzenedicarboxylic acid,



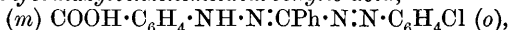
prepared from metabenzylidenehydrazobenzonic acid and diazotised orthamidobenzoic acid, separates from acetone and water as a pale red, crystalline powder melting at 225° . The acids from metamidobenzoic and paramidobenzoic acids melt at 214° and 218° respectively.

Formazylbenzenemetacarboxylic acid,



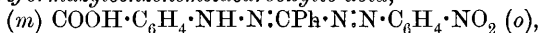
is obtained from metabenzylidenehydrazobenzonic acid and diazotised aniline; it crystallises from alcohol in beautiful, reddish-black needles, and melts at 202° . Oxidation converts it into triphenylmetacarboxy-tetrazolium chloride, which yields the iodide melting at 217° .

Orthochloroformazylbenzenemetacarboxylic acid,



crystallises from acetone in reddish-black needles and melts at 217° .

Orthonitroformazylbenzenemetacarboxylic acid,



prepared from metabenzylidenehydrazobenzonic acid and diazotised orthonitraniline, crystallises from acetone in ruby-red needles and melts at 150° . Metanitroformazylbenzenemetacarboxylic and paranitroformazylbenzenemetacarboxylic acids melt at 185° and $165\text{--}170^\circ$ respectively.

Xylylformazylbenzene, *orthotolylformazylbenzene*, and *cumidylformazylbenzene* melt at 137° , $154\text{--}155^{\circ}$, and $173\text{--}174^{\circ}$ respectively.

Methyldiphenyltetrazolium *platinochloride*, which is a yellowish powder insoluble in all media excepting phenol, blackens at 220° , and melts at $238\text{--}239^{\circ}$. M. O. F.

Action of Chlorine on Ethers of Phenol and of β -Naphthol. By A. CURATOLO (*Gazzetta*, 1898, 28, i, 154—159).—*Phenylic chlorosalicylate*, $\text{COOPh}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{OH}$ [$\text{OH}:\text{Cl}=2:5$], obtained by passing chlorine into an alcoholic solution of salol, crystallises in colourless needles melting at $81\text{--}83^{\circ}$, and on hydrolysis with potash yields 5-chlorosalicylic acid melting at 171° . On passing chlorine into an acetic acid solution of salol, *phenylic dichlorosalicylate*,

$\text{COOPh}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{OH}$ [$\text{OH}:\text{Cl}_2=2:3:5$], is obtained; this crystallises in colourless needles melting at $115\text{--}116^{\circ}$, and on hydrolysis with potash yields the 3:5-dichlorosalicylic acid melting at 214° .

Monochloro- β -naphthyllic dichlorosalicylate, $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{OOC}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{OH}$, is obtained by the action of chlorine on an alcoholic solution of betol; it crystallises in yellowish needles melting at $155\text{--}157^{\circ}$, and on hydrolysis with potash yields 3:5-dichlorosalicylic acid and 1-chloro-2-naphthol melting at $69\text{--}70^{\circ}$. Its constitution is thus defined. On chlorination in acetic acid solution, betol yields a mixture of dichloronaphthyllic 3:5-dichlorosalicylates melting sharply at $192\text{--}197^{\circ}$; on hydrolysis with potash, it yields a mixture of dichloro- β -naphthols, melting at $95\text{--}105^{\circ}$.

On chlorinating β -naphthyllic benzoate in alcoholic or acetic acid solution, a liquid *tetrachloro-derivative*, $\text{C}_{17}\text{H}_8\text{Cl}_4\text{O}_2$, is obtained; this boils at $178\text{--}180^{\circ}$, and on hydrolysis with potash yields 2:5-dichloro-1-benzoic acid. W. J. P.

Chlorine Derivatives of Phenylic Carbonate. By ETIENNE BARRAL (*Compt. rend.*, 1898, 126, 908—909).—*Chlorophenylic carbonate*, $\text{CO}(\text{OC}_6\text{H}_4\text{Cl})_2$, is obtained by placing in a large flask a solution of phenylic carbonate in carbon tetrachloride containing a small quantity of iodine, and filling the upper part of the flask repeatedly with chlorine. The reaction is somewhat energetic, but the presence of iodine is indispensable. The product, which crystallises in colourless, silky needles, melts at 142° , is insoluble in water, and only slightly soluble in cold benzene or alcohol, but very soluble in these liquids at their boiling points.

If the chlorine is passed into the carbon tetrachloride solution containing iodine (or antimony pentachloride) higher chlorine derivatives of the phenylic carbonate are produced, and these will be described later. C. H. B.

Migration of Chlorine from the Side-chain to the Ring on the Decomposition of Aromatic Iodochlorides: Derivatives of Anisidine. By PAUL JANNASCH and W. HINTERSKIRCH (*Ber.*, 1898, 31, 1710—1714).—*Orthiodanisole* is prepared from orthanisidine by the Sandmeyer reaction, and boils at $237\text{--}238^{\circ}$; its *dinitro-derivative* crystallises from alcohol in colourless, silky needles melting at 89° .

Anisole iodochloride, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{ICl}_2$, separates in lemon-yellow

crystals when chlorine is passed into a solution of iodanisole in chloroform. Hydrogen chloride is liberated spontaneously from this substance in dry air, and if decomposition is allowed to proceed in the atmosphere, it changes completely to a dark brown liquid, which crystallises if cooled artificially and stirred persistently with a glass rod; it consists of *chloriodanisole* [$\text{Cl} : \text{I} : \text{OMe} = 5 : 2 : 1$], which separates from aqueous alcohol in large, colourless crystals and melts at 48° . Chloriodanisole is also produced when anisole iodochloride is agitated with a solution of potassium iodide, one atomic proportion of iodine being set free. When chlorine is passed into a chloroform solution of chloriodanisole, the *iodochloride* of chloranisole is obtained, and crystallises from carbon bisulphide in yellow, transparent plates; when carefully dried, it may be preserved for weeks without undergoing decomposition, and chlorine does not migrate into the ring.

Iodosoanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{IO}$, prepared by the action of caustic soda on anisole iodochloride, is a colourless substance, and liberates iodine from hydriodic acid. The action of steam converts it into *iodoxyanisole*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$. M. O. F.

Migration of Chlorine from the Side-chain to the Ring on the Decomposition of Aromatic Iodochlorides: Derivatives of Phenetidine. By PAUL JANNASCH and M. NAPHTALI (*Ber.*, 1898, 31, 1714—1716).—Phenetole *iodochloride*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{ICl}_2$, decomposes spontaneously in air, yielding a pale yellow oil which boils at 273 — 278° . By the action of chlorine, this substance is converted into chlorophenetole *iodochloride*, which crystallises from carbon bisulphide in deep yellow prisms, and decomposes at 103° ; in the dry state, it is quite stable, but rapidly decomposes when exposed to moisture, hydrogen chloride being liberated. M. O. F.

Paramidophenylic Ethylenic Ether. By WILHELM KINZEL (*Arch. Pharm.*, 1898, 236, 260—262).—Paranitrophenylic ethylenic ether, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2 \text{C}_2\text{H}_4$, prepared by the action of ethylenic dibromide on the sodium compound of paranitrophenol, crystallises from glacial acetic acid in thick, pale brown needles melting at 147° . When reduced with iron and acetic acid, it yields *paracetamidophenylic ethylenic ether* melting at 257° , which, on treatment with alcoholic hydrogen chloride, gives *paramidophenylic ethylenic ether*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2 \text{C}_2\text{H}_4$, crystallising from alcohol in long, colourless needles melting at 176° ; with oxidising agents, its solutions give beautiful colour reactions. The *hydrochloride* crystallises from water in long, colourless needles melting and decomposing above 300° ; the *sulphate* forms colourless needles almost insoluble in water and alcohol and decomposing above 300° ; and the *oxalate* crystallises in fine, prismatic plates melting and decomposing at 285° . A. W. C.

Derivatives of Dinitro-orthocresol. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1897, [iii], 17, 204—206).—*Potassium dinitro-orthocresol*, $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2 \cdot \text{OK}$ [$\text{Me} : \text{OK} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 3 : 5$], obtained on adding a slight excess of potash to a boiling aqueous solution of dinitro-orthocresol, crystallises in orange-coloured spangles soluble in water and in alcohol.

Ammonium dinitro-orthocresol, $C_6H_2Me(NO_2)_2 \cdot ONH_4 + H_2O$, prepared by saturating dinitro-orthocresol with ammonia, forms golden-yellow needles soluble in water and alcohol.

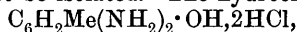
Barium dinitro-orthocresol, $[C_6H_2Me(NO_2)_2 \cdot O]_2Ba + 2H_2O$, is obtained in orange needles, soluble in water and alcohol, by decomposing barium carbonate with a boiling solution of dinitro-orthocresol.

Calcium dinitro-orthocresol, $[C_6H_2Me(NO_2)_2 \cdot O]_2Ca + H_2O$, from calcium carbonate and dinitro-orthocresol, crystallises in fine, golden-yellow needles, soluble in water and alcohol.

Acetyldinitro-orthocresol, $C_6H_2Me(NO_2)_2 \cdot OAc$, obtained by boiling acetic anhydride with dinitro-orthocresol for an hour, is a colourless compound melting at 95° , insoluble in water, but soluble in alcohol, ether, and benzene.

Nitramido-orthocresol, $C_6H_2Me(NO_2)(NH_2) \cdot OH$, is produced when dinitro-orthocresol is reduced with ammonium hydrogen sulphide. It crystallises from benzene in reddish-brown needles melting at 165° , insoluble in water, but soluble in alcohol, ether, or benzene.

Diamido-orthocresol, $C_6H_2Me(NH_2)_2 \cdot OH$, formed in the reduction of dinitro-orthocresol with tin and hydrochloric acid, is an unstable substance which could not be isolated. The hydrochloride,



crystallises in nearly colourless needles soluble in water and alcohol, insoluble in ether.

N. L.

Acylation of Alcohols and Phenols in Pyridine Solution. By ALFRED EINHORN and FRIEDRICH HOLLANDT (*Annalen*, 1898, 301, 95—115).—It has been sometimes observed that the action of benzoic chloride on polyhydric alcohols proceeds in different directions, according as pyridine or caustic soda is the medium employed. Glycerol yields the tribenzoyl derivative by both methods; the tribenzoyl derivative alone is obtained from erythritol by the Schotten-Baumann method, whilst the dibenzoyl, tribenzoyl, and tetrabenzoyl derivatives are produced in presence of pyridine. *Dibenzoylmannitol* is obtained from mannitol, using pyridine as a medium, and crystallises from alcohol in stellate aggregates of minute needles melting at 178° ; it differs, therefore, from the dibenzoylmannitol described by Meunier.

The action of acidic chlorides on such phenols as eugenol, β -naphthol, pyrocatechol, resorcinol, and pyrogallol has been also studied by the authors. The *acetyl* derivative of pyrogallol crystallises in lustrous needles and melts at 171° ; ferric chloride develops a brown coloration in the alcoholic solution. The *benzoyl* derivative of pyrogallol separates from chloroform in prisms and melts at 140° ; the *dibenzoyl* and *tribenzoyl* derivatives melt at 108° and 89° respectively. *Ethyl pyrogalloltricarboxylate*, $C_6H_3(O \cdot COOEt)_3$, obtained by the action of ethylic chloroformate on pyrogallol dissolved in pyridine, crystallises from alcohol in small prisms melting at 58 — 60° ; distillation resolves it into carbonic anhydride, ethylic carbonate, and the compound $C_6H_3O_3 : C \cdot OEt$, obtained by Bender (compare also Syniewski, *Abstr.*, 1895, 1, 602). *Ethyl pyrogalloldicarboxylate*, $OH \cdot C_6H_3(O \cdot COOEt)_2$, crystallises from water in plates and melts at 83° .

Tribenzoylgallic acid, $COOH \cdot C_6H_2(OBz)_3$, crystallises from alcohol in

small, lustrous needles, and melts at $191-192^{\circ}$; the *methylic* salt melts at 139° .

Methylic paracetamidosalicylate, $\text{COOMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NHAc}$, crystallises from alcohol in needles and melts at 147° .

When phenols are dissolved in a solution of pyridine in glacial acetic acid, treated with acetic chloride, and after an interval diluted with water, the acetyl derivative of the phenol is precipitated in quantitative amount; if benzoic chloride is substituted for acetic chloride, the same compounds are formed along with benzoic acid.

On passing carbonylic chloride into a solution of β -naphthol in glacial acetic acid containing 20 per cent. of pyridine, acetyl- β -naphthol is produced. The *propionyl* and *isobutyryl* derivatives of β -naphthol melt at 51° and 43° respectively; the *isovaleryl* derivative crystallises in long needles, and boils at $180-184^{\circ}$ under a pressure of 20 mm.

Formyleugenol is a colourless oil having the odour of eugenol; it boils at 150° under a pressure of 20 mm. The *formyl* derivative of isoeugenol boils at $155-160^{\circ}$ under a pressure of 20 mm.; both compounds yield formylphenylhydrazine when treated with aqueous phenylhydrazine hydrochloride and sodium acetate.

Orthocresol carbonate, $\text{CO}(\text{O} \cdot \text{C}_6\text{H}_4\text{Me})_2$, crystallises from alcohol in silky needles and melts at 60° . *β -Naphthyl carbonate*, $\text{CO}(\text{O} \cdot \text{C}_{10}\text{H}_7)_2$, crystallises from toluene in lustrous leaflets and melts at 178° .

M. O. F.

Methylphloroglucinol. By HUGO WEIDEL (*Monatsh.*, 1898, 19, 223—235. Compare this vol., i., 304).—*Methylphloroglucinol* is obtained as a brown, friable, crystalline mass when an aqueous solution of 2 : 4 : 6-triamidotoluene hydrochloride, heated for 30 hours with water free from oxygen, is extracted with amyl alcohol, the extract subjected to steam distillation, and the residual solution evaporated under reduced pressure. When pure, it crystallises on adding xylene to its solution in ethylic acetate in white needles which darken at $170-180^{\circ}$, and melt at $214-216^{\circ}$; it is soluble in water, alcohol, ether, ethylic acetate, and hot glacial acetic acid, but only slightly so in boiling xylene, and insoluble in benzene and light petroleum.

Methylphloroglucinol reduces ammoniacal silver nitrate in the cold, and produces violet colorations with ferric chloride and with a pine shaving moistened with hydrochloric acid; it is sweet with a bitter after-taste, and, like phloroglucinol, it reacts both as a trihydric phenol and also as a ketone.

Triacetylmethylphloroglucinol, obtained by heating methylphloroglucinol with acetic anhydride, forms an opaque, white mass of microscopic needles; it melts at 52° , dissolves readily in alcohol, ethylic acetate, benzene, and light petroleum, but is only slightly soluble in hot water.

Ethylic methylphloroglucinol carbonate, $\text{C}_6\text{H}_2\text{Me}(\text{O} \cdot \text{COOEt})_3$, separates as a heavy oil when ethylic chlorocarbonate is added to a cooled solution of methylphloroglucinol in caustic soda; it boils without decomposition at $245-248^{\circ}$ under a pressure of 17 mm. and does not solidify at 20° .

Methylphloroglucinol methylic ether, $C_6H_2Me(OH)_2 \cdot OMe$, is prepared by saturating a cold solution of methylphloroglucinol in absolute methylic alcohol with hydrogen chloride, dissolving the crystalline precipitate which forms in benzene, evaporating the solution to dryness, and distilling the residue under reduced pressure. It crystallises from xylene in lustrous, colourless needles, melts at 124° , and boils at $195\text{--}198^\circ$ under a pressure of 20 mm. It dissolves easily in alcohol and ethylic acetate, but only slightly in water and light petroleum; its aqueous solution gives no colour reactions with ferric chloride or with a pine shaving moistened with hydrochloric acid.

Methylphloroglucinol dimethylic ether, $C_6H_2Me(OMe)_2 \cdot OH$, is produced together with some monomethylic ether when the above experiment is performed on a warm solution. By crystallisation from benzene, the monomethylic ether can be separated in the crystalline state, and the mother liquor, when evaporated and distilled, yields a pasty mass from which the dimethylic ether can be separated by crystallisation from xylene as a flocculent mass of small needles; it boils at $178\text{--}180^\circ$ under 20 mm. and melts at $60\text{--}61^\circ$; it is very soluble in alcohol, ether, ethylic acetate, benzene, and xylene, but almost insoluble in petroleum and hot water.

Two monomethylic and two dimethylic ethers are theoretically possible, and the author has not yet determined the position of the methoxyl groups in the ethers described.

Methylphloroglucinol reacts with hydroxylamine, but the product has not been identified. G. T. M.

2:4-Dimethylphloroglucinol. By HUGO WEIDEL and FRANZ WENZEL (*Monatsh.*, 1898, 19, 236—246).—2:4-Dimethylphloroglucinol, prepared from the hydrochloride of 2:4:6-triamidometaxylene by the method employed in the production of methylphloroglucinol (compare previous abstract) crystallises from xylene in pale yellowish-white needles, and melts at 163° ; it is soluble in water and the usual organic solvents. When precipitated by xylene from its solution in glacial acetic acid, it contains acetic acid of crystallisation, but if the solution, placed over lime, is allowed to evaporate in a vacuum, monoclinic prisms are obtained which are free from this solvent. An aqueous solution deposits monoclinic prisms containing $3H_2O$. Dimethylphloroglucinol, like its homologues, gives characteristic colour reactions with ferric chloride and the pine shaving, and reduces ammoniacal silver nitrate in the cold; its aqueous solution is acid to phenolphthalein, and one molecular proportion of soda is required to produce neutrality.

Triacetyldimethylphloroglucinol crystallises from ethylic acetate in aggregates of lustrous needles and melts at 123° ; it dissolves with difficulty in ether, but is readily soluble in alcohol.

Ethylic dimethylphloroglucinol dicarbonate, $OH \cdot C_6HMe_2(O \cdot COOEt)_2$, obtained, like the corresponding compound, from methylphloroglucinol, is a transparent oil which solidifies on standing, but liquefies on warming to $35\text{--}40^\circ$, and boils at $242\text{--}243^\circ$ under a pressure of 16 mm. It dissolves in ether and alcohol in all proportions, but is less soluble in benzene and petroleum; from all these solvents, it separates as an oil.

Dimethylphloroglucinol methylic ether, $C_6HMe_2(OH)_2 \cdot OMe$, prepared like the corresponding derivative of methylphloroglucinol, boils at 188° under 21 mm. pressure, and crystallises from benzene in aggregates of colourless leaflets; it melts at $100-101^\circ$. This methyl derivative is readily soluble in alcohol, less soluble in water, and gives no colour reactions with ferric chloride or the pine shaving.

During the conversion of triamidometaxyline into dimethylphloroglucinol, a bye-product is obtained which is insoluble in ether and is extracted from the aqueous solution by amylic alcohol; it has the composition $C_6HMe_2(OH)_2 \cdot NH_2 \cdot HCl$, and is probably formed from a triamidometaxyline other than the 2:4:6-compound. In the preparation of 2:4:6-trinitrometaxyline, small quantities of the other two isomerides are formed, and these, on reduction, would give rise to triamidometaxylenes which might not part with all their amidogen groups on boiling with water. G. T. M.

2:4:6-Triamidotrimethylbenzene and Trimethylphloroglucinol. By HUGO WEIDEL and FRANZ WENZEL (*Monatsh.*, 1898, 19, 249-267).—The *hydrochloride of triamido-1:3:5-trimethylbenzene*, obtained by the reduction of trinitromesitylene with tin and hydrochloric acid, crystallises in small, colourless leaflets which are very insoluble in alcohol and in concentrated hydrochloric acid; when heated, the salt decomposes without melting. The free *base* crystallises from xylene in small, pale yellow needles which darken on exposure to the air; it melts at $117-119^\circ$, dissolves readily in hot water, but is only slightly soluble in benzene, light petroleum, ether, and ethylic acetate. When heated with excess of acetic anhydride, triamidotrimethylbenzene is converted into *triacetyldiamidohydroxytrimethylbenzene* $C_6Me_3(NHAc)_2 \cdot OAc$, which crystallises from xylene in clusters of needles melting at $204-205^\circ$; an alcoholic solution slightly diluted with water yields the substance in glistening prisms.

2:4:6-Diamidohydroxytrimethylbenzene hydrochloride, obtained by hydrolysing the preceding compound, crystallises from dilute hydrochloric acid in glistening needles. On long boiling with water, both the above-mentioned hydrochlorides yield trimethylphloroglucinol; this substance crystallises from glacial acetic acid or xylene in colourless needles having a silky lustre, melts at 150° , and is identical with the compound formerly obtained by O. Margulies (compare Abstr., 1889, 1153). When crystallised from an aqueous solution, it contains $3H_2O$. Trimethylphloroglucinol has a slightly bitter taste, reduces ammoniacal silver nitrate, and gives a transient colour reaction with ferric chloride, but none with the pine shaving; it is readily soluble in methylic and ethylic alcohols and ethylic acetate, and slightly in hot benzene and petroleum.

Triacetyltrimethylphloroglucinol crystallises from benzene in short, monoclinic prisms melting at 102° ; it is soluble in alcohol, ether, and ethylic acetate.

Ethylic trimethylphloroglucinol dicarbonate $OH \cdot C_6Me_3(O \cdot COOEt)_2$, is a colourless, viscid, uncrystallisable mass boiling at $230-232^\circ$ under a pressure of 14 mm. As in the case of dimethylphloroglucinol, only the dicarboxylate is obtained, even with excess of ethylic chlorocarbonate.

Trimethylphloroglucinol methylic ether, $C_6Me_3(OH)_2 \cdot OMe$, crystallises from benzene in colourless needles readily soluble in alcohol, ethylic acetate, and hot water; it melts at $120-121^\circ$ and boils at $196-198^\circ$ under 20 mm. pressure. G. T. M.

Paramidobenzaldehyde. By REINHOLD WALTHER and WILHELM BRETSCHNEIDER (*J. pr. Chem.*, 1898, [ii], 57, 535—539).—Kalle & Co., of Biebrich, have patented a method (D.R.-P. No. 89244) for the preparation of nitroparamidobenzaldehyde. No mention is made in the patent of the position of the nitro-group, but as the substance is a mono-substitution product of a para-compound, the nitro-group can only occupy the ortho- or meta-position relatively to the aldehydic group. The production of such compounds would be of great interest for the synthesis of members of the indigo group and certain dioxy-compounds.

Although the authors worked exactly according to the instructions given in the patent, they were unable to obtain a mononitro-derivative but only a *dinitramidobenzaldehyde* melting at 168° , whereas the melting point of the supposed mononitro-derivative is given at 170° . Further investigation of the substance was therefore abandoned.

The following affords a cheap means of preparing parahydroxybenzaldehyde. To a hot solution of paramidobenzaldehyde in hydrochloric acid, sodium nitrite is added, and when the reaction is ended the whole is filtered and the filtrate decomposed with sodium hydrogen sulphite, and evaporated to one-third of its volume. On cooling, parahydroxybenzaldehyde separates in silken crystals melting at $115-116^\circ$.

When a solution of the hydrochloride of paramidobenzaldehyde is treated with sodium nitrite in presence of nitric acid, *mononitroparahydroxybenzaldehyde* is obtained in good yield as yellow needles melting at $131-133^\circ$. Attempts to prepare an oxy-indigo by Baeyer's reaction by means of acetone and caustic soda failed, and therefore the substance has probably the constitution $C_6H_3(COH)(NO_2) \cdot OH$ [$= 1 : 3 : 4$]. A. W. C.

Synthesis of Aromatic Hydroxyaldehydes. By LUDWIG GATTERMANN and W. BERCHELMANN (*Ber.*, 1898, 31, 1765—1769. Compare this vol., i, 476).—The Friedel-Crafts reaction is not only applicable to phenolic ethers in the manner already described (*loc. cit.*), but may be employed in the preparation of aromatic hydroxyaldehydes from phenols, these being gently heated with hydrogen cyanide, benzene, and aluminium chloride, while a current of hydrogen chloride is passed through the liquid. The yield in many cases is almost quantitative.

1 : 4-*Hydroxynaphthaldehyde*, $OH \cdot C_{10}H_6 \cdot COH$, crystallises from dilute alcohol in pale yellow needles and melts at 181° .

1 : 2 : 3 : 4-*Trihydroxybenzaldehyde*, $(OH)_3C_6H_2 \cdot COH$, prepared by this means from pyrogallol, crystallises from water in colourless needles, and melts at $157-158^\circ$. M. O. F.

Tetramethyldiamidobenzophenone Derivatives. By EDOUARD GRIMAUZ (*Compt. rend.*, 1898, 126, 1117—1118).—The dinitro-compound, $CO(NO_2 \cdot C_6H_3 \cdot NMe_2)_2$, obtained by the action of potassium

nitrate on the ketone in presence of concentrated sulphuric acid, forms small, orange crystals which melt at 165—166°. It is probably a meta-derivative. The amido-derivative does not crystallise.

The dibromo-derivative, $\text{CO}(\text{C}_6\text{H}_3\text{Br}\cdot\text{NMe}_2)_2$, forms hard, brilliant prisms which melt at 130—131°.

Both these compounds interact with dimethylaniline and phenyl- α -naphthylamine in presence of phosphorus chlorides, yielding colouring matters which are less brilliant than those obtained with the parent substance, so that the introduction of the bromine or the nitro-group has no advantages.
C. H. B.

Reduction of Methylcyclohexenone. By CARL D. HARRIES (*Ber.*, 1898, 31, 1806—1807. Compare Knoevenagel and Tübben, *Abstr.*, 1897, i, 607).—*Diketodimethyldihexahydrophenyl*, $\text{C}_{14}\text{H}_{22}\text{O}_2$, is obtained by reducing methylcyclohexenone with alcohol and sodium amalgam in a freezing mixture; it separates from ether in slender, white needles, and melts at 160—161°. The *hydrazone* melts at 210°.
M. O. F.

Condensation of Salicylaldehyde with Acidic Amides. By FRANZ CEBRIAN (*Ber.*, 1898, 30, 1592—1604).—Under the influence of anhydrous sodium acetate, salicylaldehyde yields condensation products with acidic amides, combining with these substances in molecular proportion. The compounds obtained from this source have a

constitution expressed by the general formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CR}\cdot\text{OH} \\ \text{CH}:\text{N} \end{smallmatrix}$,

in which R represents the radicle which characterises the original amide; to substances of this type, the author gives the name *coumarazine*, in order to indicate their relation to coumarin,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CO} \\ \text{CH}:\text{CH} \end{smallmatrix}$. The coumarazines are yellow compounds, and

develop a beautiful red coloration with concentrated sulphuric acid; oxidation with potassium permanganate converts them into *coumar-*

azone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{C}=\text{O} \\ \text{CH}:\text{N} \end{smallmatrix}$, which is easily hydrolysed.

Methylhydroxycoumarazine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CMe}\cdot\text{OH} \\ \text{CH}:\text{N} \end{smallmatrix}$, is obtained by

heating an intimate mixture of acetamide (5 grams), anhydrous sodium acetate (6 grams), and salicylaldehyde (10 grams) in an oil bath at 130—140° for 2—3 hours; when water vapour is no longer set free, the product is left in contact with water (200 c.c.) during 12 hours, when it is powdered and filtered. The product, which is lemon yellow, is practically insoluble in common agents; above 150°, it gradually decomposes and becomes brown. It is insoluble in alkali carbonates, but caustic alkalis form yellow solutions which exhibit feeble reddish-violet fluorescence. If the substance is obtained by adding dilute acetic acid to a solution in alkali, it dissolves appreciably in both alcohol and acetic acid if treated with these agents while still moist. A solution in alkali, which has been exactly neutralised with dilute acetic acid, yields a white precipitate with silver nitrate, but this turns black almost immediately; lead acetate and mercuric chloride produce

yellow precipitates which become brown, whilst copper sulphate yields a greenish-white precipitate, which rapidly alters in appearance. The *barium* derivative, which is yellow, separates on adding absolute alcohol to the aqueous solution; it contains $1\text{H}_2\text{O}$, and becomes deep brown when exposed to light and air. The *acetyl* derivative, which is a snow-white powder melting at $263\text{--}264^\circ$, dissolves in alcohol, chloroform, and glacial acetic acid, and is hydrolysed by cold alkali. The *benzoyl* derivative is a white, amorphous powder, which melts and decomposes at 191° ; it dissolves in alcohol, acetic acid, and chloroform, but is insoluble in ether. The *benzylic* and *ethylic* ethers decompose at 185° and $235\text{--}240^\circ$, without previously undergoing fusion. The *nitro*-derivative, a pale-yellow, amorphous powder, dissolves in alcohol, glacial acetic acid, alkalis, and alkali carbonates; it decomposes at 75° . The *nitro*-derivative of methylacetoxycoumarazine, obtained by the action of acetic anhydride on the foregoing substance, melts and decomposes at 131° .

Coumarazone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \\ \text{CH} \end{smallmatrix} \begin{smallmatrix} \text{---} \text{C} \text{---} \text{O} \\ | \\ \text{N} \end{smallmatrix}$, prepared by oxidising methylhydroxycoumarazine in 15 per cent. sulphuric acid with potassium permanganate, crystallises from glacial acetic acid, and decomposes above 70° . Hydrolysis with alkalis converts it into orthohydroxybenzylidene-amidoformic acid, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{COOH}$, the *barium* salt of which crystallises with $3\text{H}_2\text{O}$, and is decomposed by light.

Methylhydroxycoumarazine is not easily resolved into its components. When heated with concentrated caustic potash at 150° during 5 hours, it yields ammonia, acetic acid, and the anhydride of salicylaldehyde, $\text{C}_{14}\text{H}_{10}\text{O}_3$; fusion with potash eliminates ammonia, and gives rise to salicylic acid.

Hydroxycoumarazine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \\ \text{CH} \end{smallmatrix} \begin{smallmatrix} \text{---} \text{CH} \cdot \text{OH} \\ | \\ \text{N} \end{smallmatrix}$, obtained from salicylaldehyde and formamide, is a yellow, amorphous powder readily soluble in alcohol and glacial acetic acid, and melts at 98° . The *acetyl* derivative melts at 203° , and the *ethylic* ether decomposes at 210° without previous fusion. Oxidation converts hydroxycoumarazine into coumarazone.

Phenylhydroxycoumarazine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \\ \text{CH} \end{smallmatrix} \begin{smallmatrix} \text{---} \text{C} \text{---} \text{Ph} \cdot \text{OH} \\ | \\ \text{N} \end{smallmatrix}$, which is a yellow, insoluble, amorphous powder, dissolves in alkalis, but is insoluble in alkali carbonates. The *acetyl* derivative melts at $211\text{--}212^\circ$, and dissolves readily in glacial acetic acid, chloroform, and ethylic acetate; the *ethylic* ether decomposes at 200° , but does not melt. Hydrolysis with concentrated alkali eliminates ammonia and benzoic acid from phenylhydroxycoumarazine.

M. O. F.

Synthesis of Flavone. By W. FEUERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1898, **31**, 1757—1762. Compare this vol., i, 369).—On the lines followed in recent syntheses of flavone derivatives (*loc. cit.*), the authors have obtained the parent substance from the acetyl derivative of 2'-hydroxybenzylideneacetophenone (this vol., i, 371).

2'-Acetoxylbenzylideneacetophenone, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$, crystal-

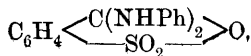
lises from dilute alcohol in small, pale yellow plates, and melts at 51—52°; the *dibromide* melts at 105—107°.

Flavone, $C_6H_4 \begin{smallmatrix} O-CPh \\ || \\ CO \cdot CH \end{smallmatrix}$, obtained by the action of alcoholic potash on the dibromide of 2'-acetoxybenzylideneacetophenone, crystallises from petroleum in aggregates of white needles melting at 97°. The solution in concentrated sulphuric acid is yellow, and exhibits very feeble blue fluorescence. The compound described by Friedländer and Neudörfer under the name flavone (Abstr., 1897, i, 425) is *benzylidene-coumaranone*, $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} C:CHPh$. Fusion with potash resolves flavone into salicylic acid and acetophenone on the one hand, ortho-hydroxyacetophenone and benzoic acid being produced at the same time (compare Abstr., 1894, i, 93). The two last-named substances are the sole products of hydrolysis with sodium ethoxide. M. O. F.

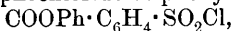
Isomeric Chlorides of Orthosulphobenzoic Acid: A Case of Tautomerism. By REINHOLD LIST and MAX STEIN (*Ber.*, 1898, 31, 1648—1672).—The crude chloride obtained by acting on orthosulphobenzoates with phosphorus pentachloride at ordinary temperatures is a mixture of two isomeric chlorides, which melt at 79° and 40°, and are produced in the proportion represented by 30—40 per cent. and 60—70 per cent. respectively (compare Remsen, Abstr., 1895, i, 472). Both chlorides are capable of action in accordance with the alternative formulæ, $COCl \cdot C_6H_4 \cdot SO_2Cl$ and $C_6H_4 \begin{smallmatrix} CCl_2 \\ \diagup \quad \diagdown \\ SO_2 \end{smallmatrix} O$, representation by rigid formulæ, and employment of the terms symmetrical and unsymmetrical, being, therefore, inadmissible. The substance melting at 79°, however, enters much more slowly into action than the isomeride; it is consequently referred to as the stable chloride, the compound which melts at 40° being called the labile chloride.

The stable chloride is prepared from the crude mixture by agitating the ethereal solution with ammonia, which attacks it very slowly, yielding orthobenzoicsulphinide; whereas the labile compound is rapidly decomposed, becoming converted chiefly into orthocyanobenzenesulphonic acid. In order to obtain the chloride of lower melting point, the mixture is distilled under reduced pressure, the stable compound being resolved into sulphurous anhydride and orthochlorobenzoic chloride. The labile substance is also the sole product when normal potassium sulphobenzoate is heated with phosphorus oxychloride at 130°. The stable chloride crystallises in the monoclinic system; $a:b:c = 1.8521:1:2.0057$. $\beta = 89^\circ 28'$. The labile compound is rhombic; $a:b:c = 1.8103:1:2.0997$. In optical characteristics, the two substances closely resemble each other. Water converts them both into orthosulphobenzoic and hydrochloric acids.

Aniline has the same action on both chlorides, yielding the symmetrical anilide, $NHPh \cdot CO \cdot C_6H_4 \cdot SO_2 \cdot NHPh$, sulphobenzanilide, $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ SO_2 \end{smallmatrix} NPh$, and the unsymmetrical anilide,



Alcohol converts the two chlorides into ethylic sulphobenzoate, $\text{COOEt} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, the chloride of this acid being the initial product in the case of the labile substance. Phenol also has the same action on both, yielding the sulphochloride of phenylic benzoate,



and diphenylic sulphobenzoate, $\text{COOPh} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Ph}$; the latter is also formed when benzene condenses with the chlorides under the influence of aluminium chloride.

Sulphobenzide is the name given by the authors to the compound, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{SO}_2 \end{smallmatrix} \text{O}$, obtained by reducing the stable chloride (compare Jones, *Abstr.*, 1894, i, 417); it crystallises from alcohol in leaflets, and melts at $112-113^\circ$. Prolonged treatment with boiling water converts it into hydroxymethylbenzenesulphonic acid; the *barium* salt crystallises in needles and contains $1\text{H}_2\text{O}$, whilst the *copper* salt, which is light blue, contains $2\text{H}_2\text{O}$. The *silver* salt forms needles.

The labile chloride, which yields thiosalicylic acid, $\text{SH} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, on reduction, softens at 158° , and melts at $163-164^\circ$. Dithiosalicylic acid is readily obtained from thiosalicylic acid on oxidation.

M. O. F.

Fluorescence of Anthranilic Acid. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, 31, 1693).—It has long been on record that aqueous solutions of anthranilic acid exhibit feeble blue fluorescence. The author has observed that solutions in alcohols, fatty acids, ketones, and ethereal salts exhibit the phenomenon distinctly, a marked violet shade being noticeable when ether, benzene, chloroform, bromobenzene, epichlorhydrin, ethylic carbonate, ethylic chloracetate, and anisole are employed. Anthranilic acid dissolved in an aqueous solution of formaldehyde gives a powerful, dark blue fluorescence, which is undiminished after exposure to light during many weeks. Solutions in *œnanthaldehyde*, oleic acid, and glycerol exhibit beautiful fluorescence, but no such effect is produced with carbon bisulphide, carbon tetrachloride, chloropicrin, formic acid, or phenylic isocyanide.

M. O. F.

Aromatic Glyoxylic Acids. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 17, 363—366. Compare *Abstr.*, 1897, i, 530).—Some improvements have been effected in the preparation of the glyoxylic acids, which are obtained by the interaction of aromatic hydrocarbons and ethylic chloroglyoxylate in presence of aluminium chloride (*loc. cit.*). It is found that the addition of nitrobenzene, in the proportion of one and a half times the weight of aluminium chloride employed, renders the action more regular, and prevents the formation of insoluble products. The alkali salts resulting from the hydrolysis of the ethereal glyoxylates are decomposed by hydrochloric acid, and the liquid shaken with ether; the residue left on evaporating the ether is dried at 100° , and the acid purified by crystallisation from hot carbon bisulphide. The glyoxylic acids are strong acids, not displaced by acetic acid; a property useful in effecting their separation from small quantities of aromatic acids, products of their decomposition, with which they are sometimes contaminated,

Attempts were made to prepare the amylic salts of various glyoxylic acids, the ethylic chloroglyoxylate being replaced by amylic chloroglyoxylate. Amylic anisoilglyoxylate and veratroleglyoxylate were readily obtained, but amylic phenylglyoxylate could not be prepared, decomposition taking place immediately, with formation of benzene and amylic chloride. Ethylic cymylglyoxylate is also unstable, and undergoes decomposition into cymene and ethylic chloride, which then interact to form ethylcymene.

The decomposition by heat of the glyoxylic acids, $R \cdot CO \cdot COOH$, takes place in two ways, with formation of aldehydes, $R \cdot CHO$, and acids, $R \cdot COOH$. The second reaction, it is now found, can be exclusively brought about by heating the acids with concentrated sulphuric acid and pouring the cooled liquid into water. The same decomposition is effected by phosphorus trichloride and oxychloride, as was discovered in attempts to prepare glyoxylic acid chlorides. N. L.

Some New γ -Ketonic Acids. By TIMOTHÉE KLOBB (*Bull. Soc. Chim.*, 1897, [iii], 17, 408—411).—The ethereal salts of the alkylphenacylcyanacetic acids, $C_6H_5 \cdot CO \cdot CH_2 \cdot CR(CN) \cdot COOH$, undergo ordinary hydrolysis in the cold, but when warmed with alkalis, γ -ketonic acids, $C_6H_5 \cdot CO \cdot CH_2 \cdot CHR \cdot COOH$, are produced, with elimination of ammonia and carbonic anhydride. The following acids were prepared in this way.

Phenacylethylacetic acid, $C_6H_5 \cdot CO \cdot CH_2 \cdot CHMe \cdot COOH$, obtained by heating methylic phenacylethylcyanacetate with the theoretical quantity of alcoholic sodium hydroxide and extracting the acidified liquid with ether, crystallises in colourless needles melting at 136° . It is insoluble in water, but soluble in most organic solvents. The potassium salt crystallises well, and is very soluble in water.

Phenacylethylacetic acid, $C_6H_5 \cdot CO \cdot CH_2 \cdot CHEt \cdot COOH$, from ethylic phenacylethylcyanacetate, forms colourless needles melting at 83° , and is no doubt identical with the acid obtained by Dittrich and Paal by the decomposition of β -benzoyl- α -ethylisosuccinic acid, and stated by them to melt at 81 — 83° .

Phenacylpropylacetic acid, $C_6H_5 \cdot CO \cdot CH_2 \cdot CHPr \cdot COOH$, crystallises in colourless needles melting at 56° . For the preparation of this acid, two hitherto undescribed ethereal salts were prepared: *methylic phenacylpropylcyanacetate* melting at 88° , and the corresponding *ethylic* salt melting at 48 — 49° .

Benzylphenacylacetic acid, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH(C_7H_7) \cdot COOH$, from ethylic benzylphenacylcyanacetate, crystallises in short, colourless prisms melting at 170° . It is insoluble in water, but more or less soluble in most organic solvents. N. L.

Caffeine Compound in Kola. Part II. Kolatannin. By JAMES W. T. KNOX and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1898, 20, 34—78. Compare this vol., i, 278).—The authors find that the tannin of the caffeine kolatannate, although not quite as light coloured as the free tannin contained in the nuts, is identical with it. The latter was obtained as follows. The sliced nuts were immersed in boiling alcohol for a few minutes, dried, ground to powder, and extracted with 50 per cent. alcohol. The alcoholic extract, concentrated in a vacuum at 18 — 20° , was filtered from the insoluble caffeine kolatannate and

colouring matter, the rest being precipitated by adding sodium chloride; the filtrate was washed with chloroform to remove fat and alkaloids, then with ether, and finally the tannin was extracted with ethylic acetate. After purifying, the kolatannin, $C_{16}H_{20}O_8$, was obtained as a cream coloured powder easily soluble in water, acetone, and alcohol, sparingly so in ether, and insoluble in chloroform and light petroleum. Its reactions closely resemble those of oak tannin. The pentacetyl derivative is a nearly white, tasteless powder, insoluble in water, sparingly soluble in ether, and easily in chloroform, alcohol, and glacial acetic acid. By the action of bromine water on an aqueous solution of the tannin, a reddish-brown, odourless, and almost tasteless tribromo-derivative is obtained, insoluble in water, ether, chloroform, and benzene, but easily soluble in alcohol and acetone.

Pentacetyltribromokolatannin, $C_{16}H_{12}Br_3(C_2H_3O)_5O_8$, prepared from the tribromo-tannin or the pentacetyl-tannin, is a tasteless, golden-yellow powder with a faint odour of acetic acid; when gently heated, it loses acetic acid, and both bromine and acetic acid on heating more strongly. A tetrabromo-derivative of the tannin, prepared by the action of bromine on an alcoholic solution of the tannin, resembles the tribromo-derivative, but is slightly darker and has a faint odour of bromine. The pentacetyltetrabromo-derivative is slightly darker than the corresponding tribromo-derivative, but otherwise closely resembles it. A pentabromo-derivative of the tannin was also obtained; it is less stable than the tetrabromo-derivative, has a stronger odour of bromine, and yields a pentacetyl derivative. By the action of a considerable excess of bromine on an alcoholic solution of the tannin, a hexabromo-derivative was prepared; this is darker in colour than the other bromo-derivatives, has a stronger odour of bromine, and yields a tetracetyl derivative. By heating the tannin at $107-110^\circ$, $135-140^\circ$, and $155-160^\circ$, the anhydrides $(C_{16}H_{19}O_7)_2O$, $(C_{16}H_{17}O_6)_2O$, and $C_{16}H_{16}O_6$ are formed respectively. The first is darker coloured than the tannin itself, and less soluble in water; the second is dark reddish-brown and insoluble in water, and the last is dark brown and insoluble in water. All the anhydrides are soluble in alcohol and in a concentrated solution of the tannin. According to the authors, an anhydride, $C_{16}H_{18}O_7$, could also probably be obtained by heating the tannin at $120-125^\circ$. Bromine derivatives of the various anhydrides are also described.

When kolatannin is boiled with dilute sulphuric or hydrochloric acid, a red or dark brown, amorphous substance is formed which, according to the authors, is probably a decomposition product and not an anhydride.

Further experiments have failed to confirm the formation of glucose when the tannin is hydrolysed, and hence the tannin is not a glucoside, as at first supposed. When the tannin is fused with potassium hydroxide, protocatechuic acid and phloroglucinol are formed, and the former acid is also obtained by heating the tannin with glycerol at $195-200^\circ$. The tannin obtained from caffeine kolatannate was found to yield the same derivatives, and to undergo the same reactions as the uncombined tannin.

Criticisms of the methods of Jean (*Rep. de Pharm.*, 1896, [iii], 7,

49) and of Carles (*J. Pharm. Chim.*, 16, 104) for the assay of kola are appended. E. W. W.

Action of Nitric Acid at the Ordinary Temperature on Certain Aromatic Amides. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1898, 17, 190—196. Compare Abstr., 1897, i, 619).—Although the mono- and di-methylamides of benzoic, phenylacetic, and phenylpropionic acids, when treated for a short time at 0° with nitric acid, yield nitrated derivatives containing the nitro-group in the nucleus, yet with nitric acid at the ordinary temperature a very different reaction takes place, and the amides become decomposed in much the same manner as described by Franchimont for the aliphatic amides.

Benzamide, phenylacetamide, and phenylpropionamide yield nitrous oxide, as also do metanitrobenzamide, paranitrophenylacetamide, and paranitrophenylpropionamide. The corresponding monomethylamides yield both nitrous oxide and methylic nitrate, and the dimethylamides yield dimethylnitramine. At the same time, the acids thus formed become nitrated, but not in the same manner as at a lower temperature.

The amides of benzoic acid yield both meta- and ortho-nitrobenzoic acid; metanitrobenzamide and its mono- and di-methyl derivatives yield metanitrobenzoic acid, but no dinitro-acids. The amides of phenylacetic and paranitrophenylacetic acids yield 2:4-dinitrophenylacetic acid melting at 160°; this acid, if heated above its melting point, or if boiled with barium hydroxide solution, loses carbonic anhydride and yields 1:2:4-dinitrotoluene [$\text{Me}:(\text{NO}_2)_2 = 1:2:4$]. The amides of phenylpropionic acid and of its paranitro-derivative yield 2:4-dinitrophenylpropionic acid (compare Abstr., 1879, 639). J. J. S.

Action of Phenylcarbimide on some Alkyloxy-acids. By EUGÈNE LAMBLING (*Bull. Soc. Chim.*, 1897, [iii], 17, 356—362).—The reaction between phenylcarbimide and certain organic acids has been found by Haller to take place in two stages, with formation of (1) anhydrides of the acids and diphenylcarbamide, which then interact to form (2) anilides, with elimination of carbonic anhydride. The author has studied the action of phenylcarbimide on methoxy-, ethoxy-, phenoxy-, thomoxy-, and eugenoxylacetic acids, α -phenoxypropionic acid, and benzoyllactic acid, but finds that, whether the reaction occurs slowly and partially at a low temperature or quickly at a high temperature, anilides are the sole product. Phenoxyacetanilide, from phenoxyacetic acid and phenylcarbimide, has been previously obtained by Fritzsche, but the following anilides have not yet been described; they have all been identified with the products of the direct action of aniline on the acids.

Methoxyacetanilide, $\text{OMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, crystallises from light petroleum in colourless needles melting at 58°, and boiling at 185—188° under 40 mm. pressure; it is soluble in hot water, alcohol, ether, and chloroform.

Ethoxyacetanilide, $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, is a yellowish oil boiling at about 185° under a pressure of 35 mm.

Thomoxyacetanilide, $\text{C}_{10}\text{H}_{13}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, forms colourless needles melting at 81°, insoluble in water, but soluble in ether, alcohol, and light petroleum.

Eugenoxyacetanilide, $C_3H_5 \cdot C_6H_3(OMe) \cdot O \cdot CH_2 \cdot CO \cdot NHPh$, separates from light petroleum in almost colourless, prismatic crystals melting at 54° .

a-Phenoxypropionanilide, $OPh \cdot CHMe \cdot CO \cdot NHPh$, crystallises from light petroleum in light scales melting at 117° .

Benzoyllactanilide, $OBz \cdot CHMe \cdot CO \cdot NHPh$, crystallises from boiling alcohol in colourless needles melting at 153° . N. L.

Action of a Solution of Hydrogen Chloride in Methylic Alcohol on the Phenylimides of Dibasic Acids. By SEBASTIAAN HOOGEWERFF and WILLEM ARNE VAN DORP (*Rec. Trav. Chim.*, 1898, 17, 197—201).—Maleinanil (Abstr., 1887, 934), when boiled with methylic alcohol containing hydrogen chloride in solution, combines with the alcohol, yielding *methylic maleinphenylamate*,
 $COOMe \cdot CH : CH \cdot CO \cdot NHPh$.

It is best obtained by dissolving maleinanil (4 grams) in absolute methylic alcohol (28 grams), adding 4 grams of methylic alcohol saturated with dry hydrogen chloride, and boiling; at the end of a few minutes, another 4 grams of the saturated solution of hydrogen chloride is added, and the mixture again boiled until it weighs 24 grams. Recrystallised from benzene, it forms colourless plates melting at $77-79^\circ$, and decomposing at $145-150^\circ$. It dissolves very readily in alcohol, acetone, and ether, fairly readily in benzene, but only sparingly in light petroleum. Boiling water transforms it first into maleinanil and then into phenylasparaginil (Anschütz and Wirtz, Abstr., 1887, 934).

Succinanil behaves in much the same way, yielding *methylic succinophenylamate*, $COOMe \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHPh$, which, when precipitated from its alcoholic solution by water, forms colourless needles melting at $97-99^\circ$ (Meulen, Abstr., 1897, i, 415).

Methylic chlorosuccinophenylamate, obtained from monochlorosuccinanil, crystallises from benzene in colourless needles and plates melting at $101-103^\circ$.

Succinimide, succinobenzylimide, camphorimide, phthalimide, and phthalanil are not acted on when boiled with methylic alcohol containing hydrogen chloride. J. J. S.

Comparison of Imido-ethers with the Rosanilines. A Reply to Miolati. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1897, [iii], 17, 373—376).—From a minute consideration of the reactions of imido-ethers and the rosanilines, the author shows that the analogy between these two classes of compounds, which has been suggested by Miolati, does not hold good. N. L.

Synthesis of Indigo Colouring Matters. By RUBIN BLANK (*Ber.*, 1898, 31, 1812—1817).—When ethylic anilidomalonate is heated, ethylic alcohol is eliminated, with production of indoxylic acid. This reaction is a general one, and affords a means of producing higher homologues of indigo.

Ethylic anilidomalonate, $NHPh \cdot CH(COOEt)_2$, obtained by the action of aniline (2 mols.) on ethylic bromomalonate, crystallises from alcohol, and melts at 45° . *Ethylic paratoluidomalonate* and *ethylic β -naphthylamidomalonate* melt at 55° and 88° respectively.

Ethylic paratolylindoxylate, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} \text{CH} \cdot \text{COOEt}$, prepared by heating ethylic paratoluidomalonate at $250\text{--}255^\circ$, melts at $155\text{--}156^\circ$; its solution in concentrated sulphuric acid is pale yellow, and becomes greenish-blue when heated, owing to the formation of paratolylindigosulphonic acid. *Paratolylindigo* is produced by hydrolysing ethylic paratolylindoxylate with boiling alkali, and passing air through the solution; it resembles ordinary indigo, but dissolves more readily.

Ethylic β -naphthylindoxylate melts at 158° ; hydrolysis followed by oxidation converts it into β -naphthylindigo (Wichelhaus, Abstr., 1894, i, 42). M. O. F.

Dimethoxydiphenyl. By PAUL JANNASCH and E. KÖLITZ (*Ber.*, 1898, 31, 1745—1746).—*Dimethoxydiphenyl*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is prepared by heating orthiodanisole, dissolved in xylene, with sodium wire, after the liquid has remained in contact with the metal for 12 hours. It crystallises from alcohol in long, white prisms, melts at 155° , and boils at $299.5\text{--}301^\circ$. M. O. F.

The Phthalein Group. By RICHARD MEYER and LEO FRIEDLAND (*Ber.*, 1898, 31, 1739—1744. Compare Abstr., 1892, 1228).—2 : 7

Dinitrofluoran, $\begin{smallmatrix} \text{CO} \cdot \text{O} \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{NO}_2) \\ \text{C}_6\text{H}_3(\text{NO}_2) \end{smallmatrix} \text{O}$, obtained by the action of nitric acid of sp. gr. 1.5 on fluoran, crystallises from glacial acetic acid in large needles melting at $261\text{--}264^\circ$. The solution in concentrated sulphuric acid is yellow, and does not exhibit fluorescence; aqueous soda is without action, but hot alcoholic potash dissolves it, forming a reddish-yellow liquid.

2 : 7-*Diamidofluoran*, $\begin{smallmatrix} \text{CO} \cdot \text{O} \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{NH}_2) \\ \text{C}_6\text{H}_3(\text{NH}_2) \end{smallmatrix} \text{O}$, prepared by reducing the nitro-compound with stannous chloride and hydrochloric acid, crystallises from hot alcohol in small, lustrous prisms or plates, which display bright colours in polarised light. It melts at $280\text{--}282^\circ$. The solution in hot, glacial acetic acid is violet, and becomes pink on cooling. Concentrated sulphuric acid dissolves it, yielding a yellow solution, which, on heating, becomes intense cherry-red, and exhibits a yellow fluorescence when cold; the solution becomes green when diluted with water, developing a deep violet coloration with excess of caustic soda. The *hydrochloride* crystallises in aggregates of minute needles, and the *stannichloride* and *mercurichloride* are also crystalline; the *platinochloride* separates in pale, yellow needles, and the *aurichloride*, which crystallises in microscopic needles, must be precipitated from solutions containing excess of hydrochloric acid, because neutral diamidofluoran hydrochloride is immediately oxidised by gold chloride.

2 : 7-*Dihydroxyfluoran* (quinolphthalein), $\begin{smallmatrix} \text{CO} \cdot \text{O} \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix} \text{O}$, is produced on boiling a solution of diamidofluoran in concentrated sulphuric acid with a 2 per cent. solution of sodium nitrite; it crystallises from dilute alcohol in microscopic rhombic plates, melts at

225—227°, and is identical with the compound prepared from phthalic anhydride and quinol.

Trinitrofluoran, $C_{20}H_9N_3O_9$, obtained from fluoran by the action of nitric acid in presence of concentrated sulphuric acid, crystallises from dilute acetic acid in needles, and melts at 250°. The solution in concentrated sulphuric acid is yellow, and does not exhibit fluorescence, but becomes dark reddish-brown when heated.

Pentanitrofluoran, $C_{20}H_7N_5O_{13}$, is prepared by heating fluoran with fuming nitric and concentrated sulphuric acids on the water bath. It crystallises in rhombic leaflets on adding alcohol to its solution in hot nitrobenzene, and separates in stellar aggregates of needles on diluting the solution in glacial acetic acid with water. The compound does not melt below 335°. When gently heated with concentrated sulphuric acid, it dissolves, the colourless solution becoming reddish-brown with rise of temperature. Alcoholic potash gives rise to a reddish-yellow solution resembling the liquid obtained from trinitrofluoran.

M. O. F.

Preparation of $\beta\gamma$ -Diphenylquinoxaline. By TR. WOLFF (*J. pr. Chem.*, 1898, 57, 546—547).— $\beta\gamma$ -Diphenylquinoxaline may be prepared by heating the hydrochloride of orthophenylenediamine with benzil; when cold, the melt is crystallised from alcohol, a 73 per cent. yield of the substance being obtained as white needles melting at 125—126°. The difference in the melting point of this compound as obtained by Hinsberg and König, 124° (*Abstr.*, 1894, i, 624), and O. Fischer, 126° (*Abstr.*, 1891, 747), is assigned by the author to the difference in the thermometer used.

A. W. C.

Azophenine. By JOHN THEODORE HEWITT and HENRY E. STEVENSON (*Ber.*, 1898, 31, 1789—1791).—The authors support the symmetrical formula employed by O. Fischer and Hepp to represent the constitution of azophenine.

M. O. F.

Syntheses in the Carbazole Group. By FRITZ ULLMANN (*Ber.*, 1898, 31, 1697—1698).—Graebe and Ullmann have shown that phenylazimidobenzene, on distillation, is converted into carbazole, nitrogen being eliminated. The following derivatives of carbazole have since been prepared by this method.

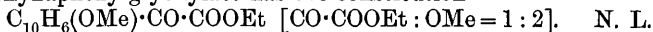
3 : 2'-Dimethylcarbazole, melting at 224°, from paratolylazimidoparatoluene; 2-chlorocarbazole, melting at 244°, from phenylazimidoparachlorobenzene; 3-amidocarbazole, melting at 235—240°, identical with the compound described by Mazzara and Leonardi; 3-methylcarbazole, melting at 207°, from paratolylazimidobenzoic acid; 1 : 2-naphthacarbazole, melting at 134.5°, described by Schöpf, and carbazole from phenylazimidobenzoic acid. 1 : 2-Naphtha-2'-methylcarbazole, melting at 181°, is obtained from *paratolylazimidonaphthalene*, which melts at 145°.

M. O. F.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Naphthalene and Naphthylic Ethers in the Presence of Aluminium Chloride. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 300—312).—The derivatives prepared from naphthalene have already been noticed (*Abstr.*, 1896, i, 652).

Ethyl chloroglyoxylate reacts with α -methoxynaphthalene in the presence of aluminium chloride to form *ethyl α -methoxynaphthylglyoxylate*, $C_{10}H_6(OMe) \cdot CO \cdot COOEt$, a white, crystalline solid, melting at 70° , and boiling at 239 — 242° under a pressure of 10 mm. It forms a yellow, crystalline *picrate* melting at 82° , and, on hydrolysis, yields *α -methoxynaphthylglyoxylic acid*, which crystallises in small, yellowish grains melting at 164 — 165° . The *methylic* salt of this acid melts at 87° . When *α -methoxynaphthylglyoxylic acid* is treated with aniline, it yields a *phenylimide* which, on heating with dilute sulphuric acid, is converted into *α -methoxynaphthaldehyde*, a white solid melting at 34° and boiling at 200 — 201° under 11 mm. pressure. This forms a *hydrazone* crystallising from benzene in yellow needles melting at 185° , and is oxidised by potassium permanganate in alkaline solution to 1:4-methoxynaphthoic acid, previously obtained by Gattermann (*Annalen*, 264, 61). It follows from these results that ethyl *α -methoxynaphthylglyoxylate* has the constitution $[OMe : CO \cdot COOEt = 1 : 4]$.

Ethyl β -methoxynaphthylglyoxylate, from ethyl chloroglyoxylate and β -methoxynaphthalene, forms colourless needles melting at 75° to a viscous liquid which boils at 235 — 238° under a pressure of 10 mm. The *picrate* crystallises in yellow needles melting at 146° . On hydrolysis, the ether yields *β -methoxynaphthylglyoxylic acid*, a yellow, crystalline solid melting at 151° , and this, on boiling with aniline, yields a *phenylimide*, boiling at 262 — 265° under 10 mm. pressure, which is decomposed by dilute sulphuric acid, with formation of *β -methoxynaphthaldehyde*. The latter crystallises from ether in hexagonal plates and from alcohol in long needles, both forms melting at 84° to a liquid which boils at 200 — 201° under 11 mm. pressure. The *hydrazone*, $C_{10}H_6(OMe) \cdot CH : N : N : CH \cdot C_{10}H_6 \cdot OMe$, forms brilliant needles melting at 265° , and *β -methoxynaphthoic acid*, obtained by oxidising the aldehyde with potassium permanganate in alkaline solution, melts at 176° . The constitution of *β -methoxynaphthaldehyde* is determined from the fact that it is identical with the product of the action of methylic iodide on the hydroxynaphthaldehyde, $[COH : OH = 1 : 2]$, obtained by Kaufmann from β -naphthol by the action of chloroform and caustic soda. Hence it follows that ethyl *β -methoxynaphthylglyoxylate* has the constitution



Alkyl Derivatives of β -Naphthol. By F. BODROUX (*Compt. rend.*, 1898, 126, 840—842).—When β -naphthol is heated with an alkyl iodide in presence of alcoholic potash, it yields compounds analogous to *β -ethoxynaphthalene*, $C_{10}H_7 \cdot OEt$, which is already known, and which forms nacreous lamellæ melting at 36° to 36.5° . *β -Propoxynaphthalene* and *β -isopropoxynaphthalene* crystallise in long, colourless needles with a penetrating and unpleasant odour; the former melts at 39.5° to 40° , and the latter at 41° . *β -Isobutoxynaphthalene* forms nacreous lamellæ which melt at 33° . *β -Isoamoxynaphthalene* crystallises from a strongly cooled alcoholic solution in white lamellæ which melt at 26.5° and boil at 315° to 316° , the distillate readily remaining in superfusion.

All these compounds combine with picric acid in alcoholic solution, and the products crystallise in long yellow or orange needles; the

propyl compound melts at 75° , the isopropyl compound at 92° , the isobutyl compound at 80° to 80.5° , and the isoamyl compound at 90.5° to 91° .
C. H. B.

Dimethyl- β -Naphthol. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 1675—1680. Compare Andreocci, *Abstr.*, 1894, i, 205).—1:4-Dimethyl-2-naphthol is obtained from santonin by converting it into desmotropo-santonin, reducing this with zinc dust and acetic acid, and fusing the product with caustic potash. As compared with β -naphthol, the substance is chemically inactive, for instance, it is incapable of yielding azo-compounds with diazonium salts; it is also indifferent towards nitrosodimethylaniline and nitrous acid. Moreover, attempts to convert it into the amine under conditions favourable to the production of β -naphthylamine from β -naphthol were fruitless. The *benzoyl* derivative crystallises from alcohol in long, colourless needles melting at 124 — 125° . The *sodium* derivative is a greyish, crystalline substance, which dissolves readily in alcohol and water. The *trinitrophenyl* ether, prepared by the action of picric chloride on the sodium derivative, crystallises from alcohol in slender, yellow needles, and melts at 189 — 190° .
M. O. F.

Ketones Derived from Naphthalene. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 313).—The compounds described in a previous communication (*Abstr.*, 1897, i, 75) have been prepared in a state of greater purity, with the result that some physical constants are slightly modified.

β -Naphthyl methyl ketone crystallises from methylic alcohol in fine, white grains melting at 53° , whilst β -naphthyl ethyl ketone, prepared in a similar manner, melts at 60° . β -Naphthyl propyl ketone crystallises from light petroleum in flat prisms melting at 52° ; and its *hydr-azone*, $C_{10}H_7 \cdot CPr:N:N:CPr \cdot C_{10}H_7$, in golden-yellow needles melting at 130° . β -Naphthyl isobutyl ketone is obtained by crystallisation from light petroleum in transparent plates melting at 36° .
N. L.

Action of α -Naphthylamine on Bromotolueneazosalicylic Acid. By JOHN THEODORE HEWITT and HENRY E. STEVENSON (*Ber.*, 1898, 31, 1785—1789).—The authors have shown that the action of aniline on orthochlorobenzeneazosalicylic acid gives rise to a compound resembling an anilide of aposafranonecarboxylic acid (*Trans.*, 1896, 69, 1257). When bromotolueneazosalicylic acid is heated with α -naphthylamine and the hydrochloride at 150 — 160° , the compound $C_{34}H_{24}N_3O_2Cl$ is produced; its constitution is probably represented by the formula $C_6H_3Me \begin{smallmatrix} \text{N} \\ \text{NCl}(C_{10}H_7) \end{smallmatrix} \gg C_6H_2(COOH) \cdot NH \cdot C_{10}H_7$. The base of which this substance is the hydrochloride has not been isolated. The *hydrobromide*, *iodide*, *nitrate*, and *sulphate* have been prepared.
M. O. F.

Preparation and Properties of Dialkylamidoanthraquinones. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1898, 126, 1544—1546. Compare this vol., i, 483).—3-Dimethylamidoanthraquinone, obtained when dimethylamidobenzoylbenzoic acid (1 part) is heated with concentrated sulphuric acid (10 parts) at 175 — 180° , crystallises

from benzene or toluene in red needles melting at 181° ; the yield is 35—40 per cent. of the theoretical, oxidation products being formed at the same time.

Dimethylamidoanthranol, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{NMe}_2$, is obtained when dimethylamidobenzylbenzoic acid is heated with 12 times its weight of concentrated sulphuric acid at 80° ; the product is poured into water and the yellow solution neutralised with sodium carbonate. The precipitate thus obtained crystallises from benzene in yellow needles. It is extremely unstable, like all anthranols, and is readily oxidised to dimethylamidoanthraquinone; the oxidising agent recommended is ferric chloride.

Diethylamidoanthraquinone, obtained from diethylamidobenzoylbenzoic acid, crystallised in red plates melting at 162° . J. J. S.

Derivatives of Fluorenone. By FRITZ ULLMANN and ED. MALLETT (*Ber.*, 1898, 31, 1694—1696).—3-Methylfluorenone, $\text{C}_6\text{H}_3\text{Me}\rangle\text{CO}$, is obtained by the action of nitrous acid on orthamidophenyl paratolyl ketone, the synthesis being analogous to the production of fluorenone from orthamidobenzophenone; it crystallises from dilute alcohol in yellow leaflets, and melts at 66.5° (corr.). A small proportion of orthohydroxyphenyl paratolyl ketone is produced along with it.

Nitrochlorobenzophenone [$\text{COPh}:\text{Cl}:\text{NO}_2 = 1:2:5$], prepared by heating the chloride of 2:5-chloronitrobenzoic acid with benzene and aluminium chloride on the water bath, crystallises from alcohol in white needles, and melts at 86° (corr.).

Nitramidobenzophenone [$\text{COPh}:\text{NH}_2:\text{NO}_2 = 1:2:5$], which is formed by the action of alcoholic ammonia on the foregoing substance, crystallises in yellowish-red prisms with blue reflex; it melts at 161.5° (corr.). 2-Nitrofluorenone, $\text{NO}_2\cdot\text{C}_6\text{H}_3\rangle\text{CO}$, is prepared by the action of nitrous acid on nitramidobenzophenone, and is identical with the product obtained by Schultz on treating fluorenone with nitric acid.

Nitrohydroxybenzophenone [$\text{COPh}:\text{OH}:\text{NO}_2 = 1:2:5$], a bye-product of the action of nitrous acid on nitramidobenzophenone, separates from alcohol in lustrous, white crystals, and melts at $124\text{—}124.5^{\circ}$.

M. O. F.

Action of the Silent Electric Discharge on Liquid Dielectrics. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 126, 691—694).—Dry terebenthene, when subjected to the action of the silent electric discharge, yields a small quantity of diterebenthene, but otherwise remains unaltered. Olive oil yields a small quantity of a blackish product insoluble in ether, oil, and all the usual solvents. Except for the difference in colour, it resembles the polymeride formed in presence of nitrogen (this vol., i, 559). Alcohol, when the action is prolonged, yields hydrogen and ethane, and the liquid contains some aldehyde and a hydrocarbon which seemingly contains less hydrogen than the olefines, and has a feeble reducing action on ammoniacal silver nitrate.

C. H. B.

Spanish Essence of Lavender. By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 378—380).—Two specimens of Spanish essence of lavender, manufactured in 1895 and 1896 respectively, were found to differ considerably in composition from the French essence. The density was higher, and the rotatory power positive instead of negative, whilst the linalol and linalol acetate, which are the essential constituents of the French essence, were replaced by borneol and a small percentage of ethereal salts. The following analytical results were obtained.

	1895.	1896.
Sp. gr. at 15°	0·916	0·912
Rotatory power	16° 25'	13° 20'
Ethereal salts, as $C_{10}H_{17}OAc$	3·15 per cent.	3·4 per cent.
Alcohols, as $C_{10}H_{17}OH$	44·5 „	50·5 „

French essence of lavender has a sp. gr. at 15° = 0·885—0·895 and a rotatory power = — 5° to — 8°. N. L.

Essence of Cedar-wood. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 485—489).—Essence of cedar-wood consists almost entirely of a liquid sesquiterpene (*cedrene*), and a solid substance (*cedrol*), having the characters of a tertiary alcohol.

Cedrene, $C_{15}H_{24}$, is a slightly viscous, colourless liquid, boiling at 131—132° under a pressure of 10 mm. It is levorotatory: $\alpha_D = -17^\circ 54'$. Cedrene absorbs bromine and halogen acids, but the compounds produced are very unstable. When oxidised by chromic acid in acetic acid solution, it yields *cedrone*, $C_{15}H_{24}O$, a liquid of ketonic character, boiling at 147—151° under a pressure of 7·5 mm.; it does not combine with sodium hydrogen sulphite, but yields iodoform with sodium hypobromite and potassium iodide so that it contains the acetyl group. It also forms an *oxime*, which boils at 175—180° under 8 mm. pressure, and is converted by acetic anhydride into an *acetate* boiling at 185—190° under a pressure of 9 mm. When reduced with sodium in ethereal solution, cedrone is converted into the alcohol *iso-cedrol*, $C_{15}H_{26}O$, which boils at 148—151° under 7 mm. pressure, and forms a *benzoate* boiling at 221—223° under 6 mm. pressure. Cedrene is oxidised by excess of chromic acid in sulphuric acid solution to a viscous *acid*, $C_{12}H_{18}O_3$, boiling at 220—230° under a pressure of 9 mm.

Cedrol, $C_{15}H_{26}O$, crystallises from methylic alcohol in colourless needles melting at 84°, and is optically active. On heating with acetic anhydride at 100°, it yields an *acetate*, $C_{17}H_{28}O_2$, boiling at 157—160° under 8 mm. pressure, and is at the same time partially dehydrated with production of a sesquiterpene; the same dehydrating action is brought about by benzoic chloride and by chromic acid. N. L.

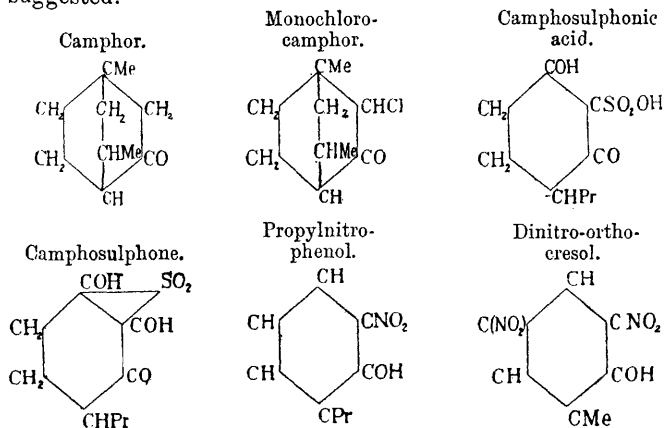
Santal Essence and its Adulteration. By W. DULIÈRE (*J. Pharm.*, 1898, [vi], 7, 332—336; from *Bull. Acad. roy. Belg.*, 1897).—The following data are given for the essence. Sp. gr. at 15 = 0·973—0·976. Solubility in alcohol at 70°, 1 part in 5 if the essence is fresh or well preserved, otherwise 1 in 15. Saponification number, maximum = 12·6. Percentage of santalol = 94. Concentrated sulphuric acid should cause solidification to a dry and friable mass. Iodine number after 3 hours = 157·6—159·25. It should give practically no coloration with

Dragendorff's reagent (bromine and chloroform), with a solution of zinc chloride in hydrochloric acid, or with Conrady's reagent. J. J. S.

Essence of Geranium. By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 489—492).—The rotatory power of a number of specimens of essence of geranium was found to be lowered by saponification, a fact which indicates the presence of lævorotatory ethereal salts. These appear to be absent from essence of palmarosa. N. L.

Semicarbazones of α -Ionone. By J. C. W. FERDINAND TIEMANN *Ber.*, 1898, 31, 1736—1739. Compare this vol., i, 376).—As already stated, purified α -ionone yields a semicarbazone which, after crystallisation from boiling petroleum, melts at 107—108°. If this compound is recrystallised several times from 60 per cent. alcohol, or repeatedly precipitated by water from its solution in strong alcohol, the *semicarbazone* which melts at 137—138° is obtained; the ketone regenerated from this by the action of alcoholic sulphuric acid is identical with α -ionone in all respects. M. O. F.

Constitution of Camphor and Derived Nitrophenols. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1897, [iii], 17, 202—204).—In order to explain the formation of nitrophenols, and more especially of dinitro-orthocresol, the author suggests a slight modification in Bouveault's formula for camphor. The following constitutional formulæ are suggested.



N. L.

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI (*Gazzetta*, 1898, 28, i, 11—18).—In face of the criticisms of Mahla and Tiemann (*Abstr.*, 1897, i, 85), the author adheres to his previous view of the constitutions of pernitrosocamphor and of isocamphor (Angeli and Rimini, *Abstr.*, 1897, i, 88). It is unlikely that pernitrosocamphor is a camphenylnitramine, because it does not react with diazomethane, although Pechmann has shown (*Abstr.*, 1897, i, 264) that nitramines react violently with this substance. W. J. P.

Nitrogen Derivatives of Santonic Acid. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 1680—1682).—Unlike santonic acid, santonic acid dissolved in alkali displays great activity towards diazonium chlorides.

The compound, $C_{27}H_{28}N_4O_4$, obtained by the action of diazotised aniline on santonic acid dissolved in caustic soda, is precipitated on adding hydrochloric acid to the solution; it crystallises from alcohol, and melts at $125-130^\circ$. The empirical formula shows that two benzeneazo-residues become attached to the santonic complex.

Reduction with stannous chloride and hydrochloric acid changes the intensely yellow colour of the compound to deep red, water precipitating a bright red substance from the liquid. M. O. F.

Action of Soluble Ferments on Gentianose. By EMILE BOURQUELOT (*Compt. rend.*, 1898, 126, 1045—1047).—The gentians contain a soluble ferment, analogous to invertin, which hydrolyses gentianose. Diastase and emulsin have no similar effect, but invertin from yeast, and the soluble ferments produced during the growth of *Aspergillus niger*, also hydrolyse the gentianose. The action of invertin is slower than with saccharose, and the hydrolysis is incomplete, whereas with the ferments from *Aspergillus*, which include ferments of polyglucoses, the hydrolysis is complete, and it would follow that the glucoses exist in the molecule of gentianose, partly as saccharose and partly as a polyglucose. C. H. B.

Products obtained by the Hydrolysis of Ouabain. By ALBERT ARNAUD (*Compt. rend.*, 1898, 126, 1208—1211. Compare this vol., i, 377).—Ouabain is only completely hydrolysed by dilute sulphuric acid (2 per cent.) after some 24 hours boiling; the two products are an insoluble resin and rhamnose, the amount of the latter being always 21.10—21.80 per cent. of the ouabain employed (calculated from the hydrated ouabain, $C_{30}H_{46}O_{12} + 9H_2O$). The amount of resin varies from 47.5 to 49 per cent. This resin, which has not been obtained in a crystalline state, is readily soluble in warm alcohol, in methylic alcohol, ether, or alkalis, and after drying at 135° in an atmosphere of carbonic anhydride has the composition $C_{24}H_{28}O_4$.

The hydrolysis of ouabain is probably represented by the equation $C_{30}H_{46}O_{12} + H_2O = C_6H_{12}O_5 + C_{24}H_{36}O_8$, the resin $C_{24}H_{28}O_4$ being obtained from the compound $C_{24}H_{36}O_8$ by the loss of $4H_2O$.

J. J. S.

Action of Alkalis on Ouabain. By ALBERT ARNAUD (*Compt. rend.*, 1898, 126, 1280—1282).—Sodium, potassium, and barium hydroxides do not hydrolyse ouabain, either in the cold or on boiling, they yield a hydrated derivative of ouabain, but no decomposition ensues; the reaction is practically the same at 140° , even with concentrated alkalis. The product, *ouabic acid*, $C_{30}H_{48}O_{13}$, is a monobasic acid capable of decomposing carbonates, reddening blue litmus, and yielding salts most of which are readily soluble in water. It is an amorphous, gummy substance which is laevorotatory, readily soluble in water or in alcohol, insoluble in ether, and melts at about 235° , but decomposes at the same time. When hydrolysed by boiling with dilute mineral acids, it yields rhamnose and a resin, probably identical with that obtained from ouabain (see previous abstract). The sodium salt, $C_{30}H_{47}NaO_{13} + 3H_2O$, and potassium salt are best obtained

by dissolving the acid in about 10 times its weight of alcohol, and then adding the requisite quantity of sodium or potassium ethoxide. The *barium*, *strontium*, and *lead* salts have also been prepared, the barium salt has a specific rotatory power $[\alpha]_D = -46.40$ at 20° . Ouabac acid can also be obtained by heating ouabain with water at 180° , but if the solutions are as concentrated as 15–20 per cent. hydrolysis also ensues. When fused with potash or soda, ouabain yields carbonic anhydride, oxalic acid, and a small quantity of resin.

J. J. S.

Pimpinellin. By G. HEUT (*Arch. Pharm.*, 1898, **236**, 162–164).—Pimpinellin, the bitter principle of the root of *Pimpinella Saxifraga*, crystallises from dilute alcohol in long, colourless, lustrous needles which melt at 106° , and not at 97° as stated by Buchheim (*Arch. Pathol.*, 1872, 37). With concentrated sulphuric acid, it gives a green coloration, and readily dissolves in dilute caustic potash, yielding a solution from which it is precipitated unchanged by carbonic anhydride; with its alcoholic solution, lead acetate gives no precipitate. Buchheim's analyses (*loc. cit.*) point to its composition being $C_{21}H_{16}O_8$, but those of the author agree more closely with the formula $C_{14}H_{12}O_5$.

Besides pimpinellin, there is present in an alcoholic extract of the root of *Pimpinella Saxifraga*, a yellow, crystalline substance which melts at 148° , resolidifies at 138° , and is not decolorised by treatment with animal charcoal.

W. A. D.

Bark of Hamamelis virginica L. By FRITZ GRÜTTNER (*Arch. Pharm.*, 1898, **236**, 278–320).—On extracting the bark of *Hamamelis virginica L.* with ether, a greenish-brown mass is obtained, which may be separated into two portions by means of light petroleum. The insoluble *wax* is still yellowish-white, even after repeated crystallisation from alcohol, and melts at 72° , whilst the soluble *fat*, which is dark green, consists principally of the ethereal salts of phytosterol, $C_{26}H_{44}O + H_2O$ (melting at 137°), and oleic and palmitic acids, together with an acid containing a higher percentage of carbon, probably stearic acid.

The bark, freed from fat, was then extracted with alcohol, and the extract treated with water, when a small quantity of insoluble phlobaphen was precipitated, and two soluble tannin substances obtained, (a) "*Glucosidetannin*" is a reddish-brown powder, soluble in hot water, and possessing a very astringent and bitter taste. When boiled with 2 per cent. sulphuric acid, it is converted into gallic acid and a sugar. (b) *Hamamelitannin*, $C_{14}H_{14}O_9 + 5H_2O$, as obtained from the bark in the ordinary manner, is an amorphous substance, but can be crystallised from dilute solutions in the form of fine, colourless needles melting at 74 – 75° , and after drying at 100° , at 115 – 117° . On further heating to 130° , the substance again becomes solid, is coloured brown at 198° , and melts and gives off gas at 220° . It is optically active $[\alpha]_D = +35.43^\circ$, and possesses all the properties of a tannin. No crystalline salts could be obtained.

On hydrolysis, hamamelitannin is entirely converted into gallic acid, thus proving that it is not a glucoside, but contains two gallic

acid residues in the molecule. It contains no methoxyl group, and phenylhydrazine is without action on it. On acetylation, it gives a rose-coloured *acetyl* derivative, and when benzoylated by Baumann's method, a *benzoyl* derivative, $C_{14}H_9Bz_5O_9$, is produced as a yellowish-white powder melting at $125-132^\circ$.

The bark also contains gallic acid and glucose in the free state.

A. W. C.

Aloes. By ALEXANDER TSCHIRCH and GULLOW PEDERSEN (*Arch. Pharm.*, 1898, 236, 200—212).—The *resin* prepared by digesting Barbadoes aloes with strong alcohol, and precipitating the filtered extract with water, forms a brownish powder which is easily soluble in alkalis, but insoluble in most organic solvents. On hydrolysis with dilute sulphuric acid, or better, with sodium hydrogen carbonate, it yields cinnamic acid, and a greyish-brown powder, *aloesinotannol*, $C_{22}H_{26}O_6$, which dissolves readily in potash, aqueous ammonia, ethylic and amylic alcohols, is nearly insoluble in ether, chloroform, benzene, and ethylic acetate, and yields a *benzoate*, $C_{22}H_{24}O_6Bz_2$. The resin of Cape aloes yields, on hydrolysis, the same aloesinotannol together with paracoumaric acid. Eigel (*Abstr.*, 1887, 1109) has stated that the latter is also formed on hydrolysing Barbadoes aloes with dilute sulphuric acid; the author, however, finds that, in this case, cinnamic acid alone is obtained.

On extracting with ether an aqueous solution of Barbadoes aloes from which the resin and barbaloin have previously been removed, an orange-yellow colouring matter is obtained which crystallises from alcohol in microscopic needles, readily sublimes, melts at 216° , and has the properties of an *emodin*, $C_{15}H_{10}O_5$. The latter is a powerful diarrhetic, and enhances the peristaltic movement; it is also present in several varieties of aloes, and on its presence Bornträger's test (*Zeit. anal. Chem.*, 1880, 165) depends. The latter apparently is not characteristic of aloes; it gives positive results with several other plants, and negative ones with Natal and Socotra aloes, which do not contain emodin; it is probably characteristic of a methylhydroxy-anthraquinone group.

Although purified barbaloin does not give the Bornträger reaction, it answers to this test after being subsequently crystallised from alcohol; this is probably due to the action of the air transforming a portion into emodin, since an appreciable quantity of the latter is formed when air is blown through a solution of barbaloin in 1 per cent. caustic potash.

Carefully purified anhydrous barbaloin melts at 147° , and has the composition $C_{16}H_{16}O_7$, ascribed to it by Groenewold (*Abstr.*, 1890, 639); it crystallises with $3H_2O$, of which two are lost at 100° , and the third when dried at $100-110^\circ$ in a stream of hydrogen. When fused with caustic potash, or heated with 10 per cent. sulphuric acid and steam blown through the mixture, an intensely black powder, *alonigrin*, $C_{22}H_{18}O_8$, is formed, which is readily soluble in alkalis, but insoluble in the ordinary organic solvents.

In conclusion, the author confirms Flückiger's formula, $C_{34}H_{38}O_{15} + 5H_2O$, for socaloin (this *Journal*, 1872, 299), obtained from *Aloe*

socotrina liquida, and gives the following analysis of a specimen of Barbadoes aloes.

Resin.	Barbaloin.	Emodin.	Ash.	Water.	Amorphous constituent, soluble in water.
12·65	12·25	0·15	1·75	10·5	62·7

W. A. D.

Oroselone and Peucedanin. By MAXIMILIAN POPPER (*Monatsh.*, 1898, 19, 268—279).—Peucedanin, from *Peucedanum officinale*, on treatment with hydrochloric acid, yields oroselone (m. p. 177°), but that obtained from *Imperatoria Ostruthium* gives rise to a totally different substance which decomposes at 240°. Imperatorin from the latter plant, and peucedanin from *Peucedanum officinale* are considered to be identical on account of their similar physical properties and composition, and because they were formerly both supposed to give oroselone and angelic acid on treatment with caustic alkalis; but Hlasiwetz and Weidel found that peucedanin, under these conditions, gave no angelic acid, and hence the identity of these two substances is open to question.

The author has prepared peucedanin from the root of *Peucedanum officinale*, and finds that the product, after crystallisation from alcohol and light petroleum, is not homogeneous, but can be separated into two constituents differing in their solubility in dry ether.

The less soluble part, after many fractional crystallisations, yields a substance having the appearance of peucedanin, but differing from it in composition and melting point. This compound, $C_{14}H_{11}O_3 \cdot OMe$, which the author proposes to call *oroselonemonomethylic ether*, melts at 105° (peucedanin prepared by Hlasiwetz and Weidel melts at 81—82°), distils without decomposition at 276—281° under 17 mm. pressure, crystallises from ether in yellowish-white needles, and dissolves in alkalis, forming a yellow solution; on treatment with hydrochloric or hydriodic acid, one methyl group is eliminated, and oroselone, $C_{14}H_{12}O_4$, is produced. The latter is identical with Hlasiwetz and Weidel's preparation, but its acetyl derivative, $C_{14}H_{11}O_3 \cdot OAc$, as prepared by the author, melts at 118°, whilst that obtained by the other investigators melts at 123°.

The more soluble part, after fractional crystallisation from benzene and ether, yields well-defined, yellowish-white prisms melting at 85—93°; the results of analysis point to its being an oroselone dimethylic ether, but a determination of methoxyl indicates that the substance, in spite of its definite crystalline form, probably consists of a mixture of mono- and di-methylic ethers of oroselone.

G. T. M.

Chloroproteinochrome. By C. BEITLER (*Ber.*, 1898, 31, 1604—1610. Compare Nencki, *Abstr.*, 1895, ii, 233).—It has been shown by Gmelin that a red colouring matter is formed on adding chlorine water to the products of the pancreatic digestion of egg-albumin; this the author calls *chloroproteinochrome*, and summarises the results of his investigation in the following terms. 1. The albumin molecule contains a complex, chromogenic group which is set free by

pancreatic digestion, and is precipitated by chlorine water in the form of a red chloro-compound. 2. Chloroproteinochrome, the product of this action, appears to have the composition expressed by the formula $C_{96}H_{116}Cl_3N_{21}O_{31}S$; it is decomposed by cold solutions of alkalis and metallic salts, and also by boiling alcohol and ethylic acetate, yielding indefinite substances. 3. The proteinochromogen, being represented by the approximate formula $C_{96}H_{119}N_{21}O_{31}S$, contains a larger proportion of carbon, and smaller proportions of nitrogen and hydrogen, than proteid substances; it is likewise very unstable, but diffuses through membranes, and is precipitated from aqueous solution by phosphotungstic acid, but not by metallic salts. The proteinochromogen cannot, however, be obtained by decomposing the substance which it yields with phosphotungstic acid. M. O. F.

Antimony Pentafluoride and some of its Double Salts with Organic Bases. By PAUL REDENZ (*Arch. Pharm.*, 1898, 236, 263—277).—When antimonious acid is dissolved in pure hydrofluoric acid, and the solution evaporated, a very hygroscopic, syrupy mass is left which is not completely soluble in water; neither by this method nor by dissolving antimonious oxide in hydrofluoric acid could a crystalline antimony pentafluoride be obtained. For the preparation of the following substances, a solution of antimony pentafluoride was obtained from the firm of de Haen in Hanover.

Antimony pentafluoride pyridine hydrochloride, $SbF_5 \cdot C_5NH_5 \cdot HCl$, obtained by evaporating a solution of antimony fluoride in pyridine hydrochloride, forms glistening needles melting at $176-177^\circ$; it is decomposed by water and alcohol. A second compound, probably of the formula $2SbF_5 \cdot 5(C_5NH_5 \cdot HCl)$, crystallising in rhombohedra, and melting at 180° , was also obtained. The estimation of antimony was done electrolytically, by warming the double salt with caustic soda, to get rid of pyridine, adding sodium sulphide solution, and electrolysing: and the fluorine was determined by Oettel's method (*Zeit. anal. Chem.*, 25, 505).

Antimony pentafluoride picoline hydrochloride, prepared in a similar manner, crystallises in glistening needles melting at 117° ; the *collidine hydrochloride* compound is a yellow, crystalline precipitate, whilst the *quinoline hydrochloride* compound crystallises in glistening, silky needles melting at 200° .

With paratoluidine hydrochloride, two compounds are obtained, the one, $2SbF_5 \cdot 5(C_6H_4Me \cdot NH_2 \cdot HCl)$, crystallising in needles and decomposing at $100-110^\circ$, and the other, $3SbF_5 \cdot 7(C_6H_4Me \cdot NH_2 \cdot HCl)$, in leaflets melting at 232° .

Nicotine and coniine hydrochlorides give no crystalline compounds with antimony pentafluoride.

The compound with quinine hydrochloride forms lemon-yellow crystals soluble in hot water without decomposition and melting at $213-214^\circ$. A. W. C.

Morpholine Bases. By LUDWIG KNORR (*Annalen*, 1898, 301, 1—10. Compare Abstr., 1889, 1218, and 1897, i, 314).—Morpholine, C_4NOH_9 , which is a colourless, limpid, alkaline liquid having the

odour of ammonia and piperidine, is excessively hygroscopic, and is very volatile in atmospheres of ether and water vapours. It is miscible in all proportions with common solvents, and develops heat when dissolved in water; the solution affects the skin like caustic potash, and at high temperatures will attack glass. The base boils at 128—130°, and has a sp. gr. = 1·0007 at 20°/4°; the refractive index $[n]_D = 1·4540$, whence the molecular refraction 23·54. Morpholine absorbs moisture and carbonic anhydride from the air, and fumes in moist air; carbonic anhydride precipitates the *carbamate*, $\text{OH} \cdot \text{CO}(\text{C}_4\text{H}_8\text{ON})_2$, in white crystals from the ethereal solution of the base.

The *hydrochloride* is readily soluble in water, and melts and decomposes at 174—177°; the *aurochloride* and *platinochloride* melt and decompose at 240° and 210° respectively. The *picrate* and *picrotonate* dissolve with difficulty in water, and melt at 145—147° and 255° respectively. Aqueous morpholine yields precipitates with many of the agents used for recognising alkaloids.

Nitrosomorpholine, which melts at 29°, and boils at 224—224·5° under a pressure of 747 mm., has the odour of nitrosopiperidine, and gives Liebermann's reaction. *Benzoylmorpholine* crystallises from ether in prisms, and melts at 74—75°. Morpholine *urethane* boils at 220—221° under a pressure of 746 mm.; the *carbamide* derivative melts at 110—113°.

Hydroxyethylmorpholine, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{O}$, is prepared by the action of ethylenic oxide on morpholine, and also by heating triethanolamine (trihydroxytriethylamine) with 70 per cent. sulphuric acid at 160—170°; it boils at 227°.

Morpholine is indifferent towards water at 200°, 10 per cent. caustic soda and concentrated hydrochloric acid at 160°, and phenylhydrazine at 200°; it undergoes slow oxidation with acid solutions of potassium permanganate, changing more rapidly in presence of acids.

M. O. F.

1-Methylmorpholine. By LUDWIG KNORR and HERMANN MATTHES (*Annalen*, 1898, 301, 10—14).—1-Methylmorpholine, prepared by heating diethanolmethylamine (this vol., i, 399) with 70 per cent. sulphuric acid at 160° during 16 hours, is a colourless, limpid, volatile liquid, having a powerful ammoniacal odour. The base boils at 115—116° under a pressure of 750 mm., and has a sp. gr. = 0·9051 at 20°; the refractive index $[n]_D = 1·4332$, whence the molecular refraction 29·01. Methylmorpholine is indifferent towards methylamine solution at 180°, and 30 per cent. hydrochloric acid at 250°; hydriodic acid and ammonium iodide at 240° regenerate morpholine. The ordinary alkaloid reagents yield characteristic precipitates with the base.

The *picrate*, which is almost insoluble in alcohol and ether, melts at 225—226°. The *ethiodide* is excessively hygroscopic, and melts at 165—166°.

M. O. F.

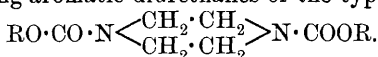
1-Ethylmorpholine. By LUDWIG KNORR and WERNER SCHMIDT (*Annalen*, 1898, 301, 14—18).—1-Ethylmorpholine, prepared by heating diethanolethylamine (this vol., i, 399) with 70 per cent. sulphuric

acid at 160° during 18 hours, is a colourless, limpid oil having a powerful ammoniacal odour; it boils at 138—139° under a pressure of 751 mm., and has a sp. gr. = 0.8996 at 20°/4°; the refractive index $[n]_D = 1.4400$, whence the molecular refraction 33.758. Alkaloid reagents give characteristic precipitates. The *hydrochloride* is colourless and hygroscopic; the *picrate* and *platinochloride* melt at 189—190° and 197—198° respectively. The *aurochloride* crystallises in golden prisms containing 1H₂O and melting at 86—89°; in the anhydrous condition it melts at 125°. The *methiodide* is identical with the ethiodide of methylmorpholine described in the foregoing abstract; the *methoxide* is an oil which yields aldehyde spontaneously.

A tabular comparison of the three morpholine bases is appended to the paper.

M. O. F.

Dimethylpiperazine and its Phenolic Derivatives. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1898, 126, 1573—1575).—It has been previously shown that piperazine reacts with phenolic carbonates yielding aromatic diurethanes of the type



Dimethylpiperazine, however, behaves in quite a different manner, carbonic anhydride being evolved and a diphenolic derivative of the type $\text{OH} \cdot \text{R} \cdot \text{NH} \left\langle \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \right\rangle \text{NH} \cdot \text{R} \cdot \text{OH}$ formed.

Dimethylpiperazine diphenate, obtained by heating the base and phenyl carbonate in molecular proportion with alcohol (93 per cent.) for three-quarters of an hour, crystallises in hard crystals when the solution is concentrated to about one-third. It dissolves in water, alcohol, ether, benzene, nitrobenzene, or glycerol, melts at 86°, and yields phenol when treated with acids.

Dimethylpiperazine diguaiacolate crystallises in fine, light needles melting at 66—67°.

Dimethylpiperazine di- α -naphthate is soluble in warm water, also in alcohol, chloroform, or nitrobenzene, but only sparingly in ether or benzene, and melts at 147°. The *β -naphthate*, which is much more soluble in alcohol than the *α -compound*, melts at 93°.

The authors question the constitution usually assigned to dimethylpiperazine.

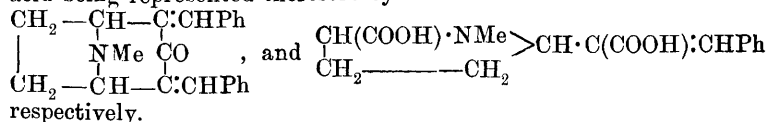
J. J. S.

Tropinepinacone. By RICHARD WILLSTÄTTER (*Ber.*, 1898, 31, 1672—1675).—In preparing large quantities of ψ -tropine by reducing tropinone with sodium or sodium amalgam, this substance is obtained as a bye-product.

Tropinepinacone, C₁₆H₂₈N₂O₂, which is insoluble in cold water, and dissolves with extreme difficulty even in boiling water, crystallises from alcohol in lustrous, four-sided plates and elongated prisms; it melts at 188°, distils without decomposing, and can be sublimed. The *hydrochloride* dissolves very readily in water, and the *mercurichloride*, which is almost insoluble in cold water, crystallises from the hot solution in thin, lustrous needles. The *platinochloride*, when crystallised slowly, separates in four sided plates containing 2H₂O; it melts and

decomposes at 275°. The *aurichloride* melts and effervesces at 228—229°, and the *picrate* decomposes above 300°. M. O. F.

Benzylidenetropinic Acid. By RICHARD WILLSTÄTTER (*Ber.*, 1898, 31, 1587—1592. Compare this vol., i, 159).—Oxidation with chromic and sulphuric acids converts dibenzylidenetropinone into benzylidenetropinic acid, which is dibasic and unsaturated; the production of this compound is regarded by the author as confirming the view that tropinic acid contains an acetic acid residue (*loc. cit.*); its unsaturated character indicates the presence of the group $C:CHPh$ in dibenzylidenetropinone, the latter substance and benzylidenetropinic acid being represented therefore by the formulæ



Dibenzylidenetropinone is prepared from tropinone and benzaldehyde more conveniently by the agency of alcoholic soda than with hydrochloric acid. Owing to the highly stable and sparingly soluble character of dibenzylidenetropinone *chromate*, which separates in microscopic, yellow prisms during oxidation, this operation must be conducted under specific conditions.

Benzylidenetropinic acid, $C_{15}H_{17}NO_4$, dissolves in 12 parts of cold, 3 parts of hot water, and crystallises in colourless, lustrous prisms containing $1H_2O$; it melts and begins to decompose at 190—191°, and is extremely hygroscopic in the anhydrous state. It dissolves with difficulty in hot acetone and alcohol, is scarcely soluble in chloroform, and insoluble in ether; the aqueous solution readily dissolves silver oxide, yielding a metallic mirror when gently heated. Both acid and alkaline solutions of benzylidenetropinic acid immediately decolorise potassium permanganate, when the odour of benzaldehyde becomes perceptible; lead peroxide liberates carbonic anhydride from the aqueous solution. The *hydrochloride* dissolves with difficulty in cold alcohol, but is freely soluble in water; it crystallises in prisms, and melts and decomposes at 244°; the *hydrobromide*, which crystallises from water in lustrous prisms and small, four-sided plates, melts and decomposes at 252—253°. Gold chloride yields the *aurichloride*, $(C_{15}H_{17}NO_4)_2 \cdot HAuCl_4$, which crystallises in yellow, anhydrous leaflets, and decomposes at 192—193°; when this substance is recrystallised several times, the *aurichloride*, $C_{15}H_{17}NO_4 \cdot HAuCl_4$, is obtained as an oil which slowly crystallises in prisms. The *methylic* salt dissolves readily in alcohol, wood spirit, and acetone, separating in thin leaflets and flattened needles on addition of water; it melts at 67—69°.

M. O. F.

Alkaloids of Corydalis. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, 236, 212—214).—Experiments carried out, at the author's suggestion, by W. H. Martindale, show that dehydrocorydaline (compare Ziegenbein, *Abstr.*, 1897, i, 175, and Dobbie and Marsden, *Trans.*, 1897, 657) can be conveniently prepared by adding bromine dissolved in

alcohol to an alcoholic solution of corydaline, and crystallising the resulting *perbromide*, $C_{22}H_{23}NO_4 \cdot HBr \cdot Br_2$, from boiling alcohol. The formation of an optically inactive corydaline by the reduction of dehydrocorydaline (Dobbie and Marsden, *loc. cit.*) is confirmed by the author; *i*-corydaline differs from natural corydaline in the greater ease with which its salts crystallise, and in yielding an *aurichloride*, $C_{22}H_{27}NO_4 \cdot HAuCl_4 + 4H_2O$, of normal composition, that obtained from natural corydaline having the abnormal constitution $(C_{22}H_{27}NO_4 \cdot HCl)_2 \cdot AuCl_3$. Attempts to resolve *i*-corydaline into its optically active components, by means of its thiocyanate (compare Davis, *Abstr.*, 1897, i, 174), failed.

From Ziegenbein's results (*loc. cit.*), the author concludes that, of the alkaloids of *Corydalis cava*, only corydaline and corybulbine are closely related; and that the views of Freund and Josephi (*Abstr.*, 1894, i, 100) as to the relationship of corydaline and bulbocapnine are incorrect. In support of this opinion, Herzig and Meyer's statement (this vol., i, 53) that bulbocapnine contains one $N \cdot CH_3$ group, whilst in corydaline this group is absent, is quoted. W. A. D.

Corydaline. By W. H. MARTINDALE (*Arch. Pharm.*, 1898, 236, 214—246).—The corydaline used was prepared from the bulbs of "*Corydalis cava*" according to methods previously described, 10 kilograms of the bulbs yielding 90 grams of the alkaloid in colourless, prismatic crystals melting at 134—135°.

The following salts were prepared in order to compare their properties with those of inactive corydaline, and also on account of the different properties ascribed to them by various investigators.

The hydrochloride obtained by passing hydrogen chloride into an ethereal solution of the base is a viscid, green mass, crystallising with difficulty from alcohol, and then containing $1C_2H_6O$, or from water when it contains $2H_2O$.

The hydrobromide, hydriodide, nitrate, and aurichloride, have the properties ascribed to them by Ziegenbein (*Abstr.*, 1897, i, 175); the acid sulphate, $C_{22}H_{27}NO_4 \cdot H_2SO_4 + 4H_2O$, obtained by dissolving the base in dilute sulphuric acid, forms groups of transparent plates; the platinochloride melts at 227°; and the thiocyanate, produced by adding thiocyanic acid to an alcoholic solution of the base, crystallises in plates melting at 208° and becoming green on exposure to the air.

Dehydrocorydaline hydriodide, $C_{22}H_{23}NO_4 \cdot HI + 2H_2O$, prepared according to Ziegenbein's directions (*loc. cit.*), forms lemon-yellow, transparent, prismatic plates easily soluble in hot water.

i-Corydaline, obtained by reducing the last-named compound with zinc and sulphuric acid, separates from alcohol in transparent, prismatic crystals melting at 135°. It is inactive, tasteless, and more stable on exposure to air than corydaline itself.

The *hydrochloride*, $C_{22}H_{27}NO_4 \cdot HCl + 2H_2O$, forms efflorescent, highly refractive, prismatic crystals; the dried salt melts at 230—240°; the *hydrobromide* is crystalline, melting and decomposing at 200°; the *nitrate* separates from alcohol in clusters of small, yellow needles; the *sulphate*, $C_{22}H_{27}NO_4 \cdot H_2SO_4 \cdot 2H_2O$, forms transparent plates, the *aurichloride*, $C_{22}H_{27}NO_4 \cdot HAuCl_4 + 4H_2O$, easily soluble, yellow needles, and

the *platinochloride*, microscopic crystals melting at 230° . The *thiocyanate*, obtained by the action of thiocyanic acid on an alcoholic solution of the base, forms transparent crystals melting at 205° and becoming green on exposure to air or light. It could not be separated into left- and right-handed modifications, as in the case of *i*-lupanine (compare Davis, Abstr., 1897, i, 174).

i-Corydaline methiodide crystallises in plates melting at 185° , and is converted by the action of excess of silver chloride into the *methochloride*, crystallising in yellow needles. Its *aurichloride* forms glistening, dark-red crystals melting at 170 – 172° , and its *platinochloride* pale yellow needles melting at 222° .

When the methochloride is acted on with sodium hydroxide, it is converted into *methyl-i-corydaline*, $C_{22}H_{26}MeNO_4$, forming flakes or brown, oily drops, which solidify when cooled; from alcohol, it may be obtained in transparent crystals melting at 224° . The *hydrochloride* crystallises with $3H_2O$ in transparent prisms, and yields an *aurochloride* melting at 205° , and a *platinochloride* melting at 220° .

A table is given containing the melting points and other characteristic properties of the natural and inactive varieties of corydaline and of methylcorydaline.

Dehydrocorydaline hydrogen hexasulphide, $(C_{22}H_{23}NO_4)_2H_2S_6$, obtained by the action of ammonium sulphide on dehydrocorydaline hydriodide, forms small, brown, glistening needles, and behaves like berberine and strychnine hexasulphides on treatment with mineral acids.

The action of bromine on an alcoholic solution of corydaline gives rise to a *perbromide* of dehydrocorydaline hydrobromide, $C_{22}H_{23}NO_4 \cdot HBr \cdot Br_2$, which, on boiling with alcohol, loses bromine, and is converted into dehydrocorydaline hydrobromide.

Dobbie and Lauder (Trans., 1894, 65, 57), by the action of potassium permanganate on corydaline, obtained a substance which they called corydalinic acid. The author has been unable to corroborate this result, and could only obtain hemipinic acid; the existence of corydalinic acid is therefore doubtful.

A. W. C.

The Alkaloids of *Macleya cordata* R. Br. By K. HOPFGARTNER (*Monatsh.*, 1898, 179–210).—The extract obtained from the stem and leaves of *Macleya cordata* contains two alkaloids, macleiyne or protopine and β -homochelidonine. Sanguinarine, which was found along with macleiyne in the roots of this plant by Eijkman (*Rec. trav. Chim.*, 3, 182), does not appear to occur in the leaves and stem. The substance described by Eijkman as macleiyne appears to be in all respects identical with the protopine obtained by various investigators from different species of *Papaveraceæ*; it melts at 207° , does not contain a methoxy-group, and has the formula $C_{20}H_{19}NO_5$, whereas the protopine from *Chelidonium* (König) and that from *Sanguinaria* (Tietz and König) have, according to these authors, the formula $C_{20}H_{17}NO_5$. With methylic iodide, it yields a *methiodide*, $C_{20}H_{19}NO_5 \cdot MeI$, which crystallises in thick, compact prisms, and gives a strongly alkaline solution when treated with silver oxide. The corresponding *metho-nitrate*, $C_{20}H_{19}NO_5 \cdot MeNO_3$, crystallises in white, silky needles. Potassium permanganate readily attacks protopine in

acid solution, but the only product which could be isolated was formic acid. On reduction with sodium amalgam, the alkaloid yields a substance which crystallises in colourless four-sided tablets, has an alkaline reaction, melts at 148° , and yields a violet-red coloration with sulphuric acid which passes into blue. The formula is probably $C_{18}H_{21}NO_4$, but has not been definitely ascertained.

The second alkaloid, the nitrate of which is much more readily soluble than that of protopine, is identical in properties with the β -homochelidonine which was obtained by Selle from *Chelidonium majus* (Abstr., 1891, 229). This base has the formula $C_{21}H_{23}NO_5$ (Selle gives $C_{21}H_{21}NO_5$), and melts at 157 — 158° , but when kept at this temperature for some time it solidifies again, and then melts at 166 — 167° . The nitrate, $C_{21}H_{23}NO_5 \cdot HNO_3 + 1\frac{1}{2}H_2O$, crystallises in spherical groups of needles, and the hydrochloride, $C_{21}H_{23}NO_5 \cdot HCl + 1\frac{1}{2}H_2O$, in slender, white needles, which are only moderately soluble in cold water. The platinochloride has not been obtained in the crystalline state, but the hydrobromide, $C_{21}H_{23}NO_5 \cdot HBr + 1\frac{1}{2}H_2O$, closely resembles the hydrochloride, and the hydriodide, $C_{21}H_{23}NO_5 \cdot HI + H_2O$, crystallises in small, white needles. A. H.

Presence of an Alkaloid in Natural Wines. By GABRIEL GUÉRIN (*J. Pharm.*, 1898, [vi], 7, 323—324).—A number of natural wines contain a small quantity of a substance of alkaloidal nature, which is probably identical with that described by Oser as formed during the fermentation of sugar by yeast (*Bull. Soc. Chim.*, 1868, [i], 10, 295.

J. J. S.

Gelatinous Matter (Pectin) in Gentian Root. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 7, 473—479. Compare Poumarède and Figuier, *ibid.*, 1847, [iii], 12, 81).—The gelatinous matter cannot be extracted by cold water, either from the dried or from the fresh root; water at 70 — 100° , however, dissolves out the gelatinous matter in a hydrated form (pectin); boiling 80 per cent. alcohol also serves to render the gelatinous matter soluble in water. A 1 per cent. solution of the pectin is gelatinised by a solution of pectase within 40 minutes, it is also readily gelatinised by lime water, or by the addition of sodium hydroxide followed by hydrochloric acid. Lead acetate, basic lead acetate, or ferric chloride bring about the same result. The solution yields no precipitate when saturated with sodium sulphate, but is precipitated by magnesium or ammonium sulphate. It has no reducing properties, but is dextrorotatory; $[\alpha]_D = +82.3^{\circ}$. Acidified water at 80° also extracts a pectin which is partly soluble in water, and which is more dextrorotatory than the one mentioned above; $[\alpha]_D = +145.3^{\circ}$. J. J. S.

Hepatic Pigments in Vertebrates. By A. DASTRE and N. FLORESCO (*Compt. rend.*, 1898, 126, 1221—1223).—Two pigments, for which the names *ferrin* and *cholechrome* are proposed, were extracted by various methods from fresh liver which had been freed from blood. Ferrin is a ferruginous albuminoid compound closely connected with the ferratin of Marfori and Schmiedeberg. It is readily soluble in

water and in dilute acids and alkalis, but insoluble in alcohol and chloroform. Cholechrome, on the other hand, is soluble in chloroform, but insoluble in water; it is intermediate in character between the lipochromes and biliary pigments. The absorption spectra of these pigments show no definite bands. N. L.

Decomposition of Elastin by Hydrochloric Acid. By EBBE BERGH (*Zeit. physiol. Chem.*, 1898, 25, 337—343; SVEN G. HEDIN, *ibid.*, 344—349).—Elastin was prepared from *ligamentum nuchæ*, and from the aorta; elementary analysis of several preparations, given in full, shows that it contains sulphur. On decomposition with hydrochloric acid, it yields neither lysine nor arginine.

Hedin's paper is confirmatory of the foregoing; histidine is also absent from the products. If Kossel's recent classification of the proteids be accepted, a new class must be provided for elastin.

W. D. H.

Action of Peptic Digestion on Proteids. By F. UMBER (*Zeit. physiol. Chem.*, 1898, 25, 258—282).—The majority of previous observers have investigated the action of pepsin-hydrochloric acid on impure proteids like fibrin. In the present research, crystalline egg-albumin, crystalline serum-albumin, and serum-globulin were employed. Attempts to crystallise serum-globulin failed; the material was prepared from blood-plasma after separation of the fibrinogen by half saturation with ammonium sulphate. In separating out the products of digestion, Pick's method of fractional precipitation with ammonium sulphate was used. Fraction 1 contained the primary proteoses; fractions 2, 3, and 4 contained three varieties of deuteroproteose, A, B, and C respectively. The peptone remaining in solution was precipitated by iodine; the iodine compound is partly insoluble in alcohol (peptone A), and partly soluble (peptone B).

The reactions of each are described, the test for sulphur, Millon's reaction, the xanthoproteic reaction, and Molisch's reaction being principally used. All the substances except peptone B gave Molisch's reaction, which is considered to indicate the existence of a carbohydrate radicle in the proteid. In all cases, too, with the exception of the two peptones, the test for loosely combined sulphur was positive.

W. D. H.

Decomposition of Proteid from Conifer Seeds. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1898, 25, 360—362).—Previous work has shown that the proteid matter from the seeds of the fir and pine yields about 10 per cent. of arginine. This is extremely high; Hedin obtained only 2.75 per cent. of this base from conglutin, and less from other proteids.

It was considered desirable to repeat this; the proteid was prepared from fir seeds by extraction with 10 per cent. solution of sodium chloride, instead of the dilute alkali previously employed. It contains 18.69 per cent. of nitrogen; this number is high; on decomposition, the amount of bases obtained exceeded that previously recorded; in fact, 34.7 per cent. of the nitrogen was obtained in the form of organic bases precipitable by phosphotungstic acid.

W. D. H.

Halogen Derivatives of Albumin. By F. BLUM and WILHELM VAUBEL (*J. pr. Chem.*, 1898, [ii], 57, 365—396).—Proteids have an especial affinity for the halogen elements: for example, egg-albumin reacts with a halogen as soon as the two are brought into contact, an intramolecular substituted proteid being produced, along with considerable amounts of a halogen acid; by removing the latter, the proteid is rendered capable of undergoing further substitution, and if the reaction takes place in neutral solution, compounds are finally produced containing a constant and definite amount of halogen.

The method of procedure is, roughly, as follows. The purified albumin is heated with iodine in sodium hydrogen carbonate solution at a temperature of 50° for 4—5 hours, and the excess of iodine is then removed by shaking with sodium hydroxide solution. Egg-albumin, casein, myosin, "somatose," nuclein, and an iodised proteid derived from the thyroid gland were treated in this manner, the products obtained being for the most part tasteless and odourless yellow powders, insoluble in water and absolute alcohol, and containing from 6—7 per cent. of iodine. They did not give Millon's reaction, but did give the biuret reaction.

Bromination and chlorination may be carried out in a similar manner. The brominated egg-albumin and casein derivatives are colourless, or grey-brown, tasteless substances, containing 4—5 per cent. of bromine; the corresponding chlorine derivatives are also tasteless and colourless or brownish compounds, containing about 2 per cent. of chlorine.

The halogens may also be introduced into proteids by means of the electric current, and this is especially useful in the case of fluorine, where substitution takes place on electrolysing a solution of egg-albumin in ammonium fluoride.

When a proteid is treated with alkali, it is decomposed into (*a*) principally a basic portion containing ash; (*b*) a portion precipitated by acids, which gives both Millon's and the biuret reactions; (*c*) a portion precipitated by alcohol, giving Millon's reaction markedly and the biuret action feebly; and (*d*) a portion soluble in absolute alcohol, containing a high percentage of sulphur and smelling like mustard oil, and this also gives the biuret reaction. The halogen proteids are decomposed in a similar manner, the same products being obtained when the halogen compounds are heated with alkalis, or when the proteid is first decomposed, and the products treated with a halogen in the manner already described.

On comparing the properties of the original and decomposed products, it is noticed that the percentage of oxygen and the acid character increases in the latter, whereas the amount of sulphur decreases, and this element may be entirely absent. The amounts of carbon, hydrogen, and nitrogen remain about the same, but the percentage of halogen in the decomposition products is almost twice as great as in the original substance; this fact affords a means of determining the amount of decomposition that has taken place. Whereas the original substances are tasteless and insoluble in water and alcohol, the products of decomposition have a slightly bitter taste, and are easily soluble in 80 per cent. alcohol.

From an investigation of a large number of substituted phenol derivatives with regard to their capability of giving Millon's reaction, the authors conclude that at least two halogen atoms enter the albumin molecule, and occupy the ortho-positions relatively to the hydroxyl-group of that benzene ring, which, on decomposition, forms tyrosine. No halogen enters the other rings of the albumin molecule.

It appears, also, that there are two groups in the albumin molecule capable of producing the biuret reaction, the activity of one of these groups being destroyed during the action of a halogen.

The relation of the molecular weights of the different proteids to their products of decomposition may be obtained by preparing the fully substituted halogen products, since the capability of combining with the halogens increases with the amount of decomposition. Presuming that two halogen atoms enter the molecule of albumin, the following molecular weights are obtained. Egg-albumin and casein = 3600; myosin = 2300; nuclein = 3600; albumoses, peptones, and other decomposition products = 1700—2540.

In conclusion, the authors point out that reactions similar to the above must take place in living organisms, halogenised proteids appearing as intermediate or final products. Experiments made with "iod-," "brom-," and "chloralbacid" show that whenever a halogen is free in the organism, halogen acids and halogenised proteids are formed, to be again decomposed as soon as they come in contact with the oxidising agents of the organism, and, therefore, such compounds have a particular physiological and therapeutical interest as halogen carriers.

A. W. C.

Behaviour of Vitellin in Magnesia Mixture. By WACŁAW VON MORACZEWSKI (*Zeit. physiol. Chem.*, 1898, 25, 252—255).—The author has previously shown that in an ammoniacal solution of magnesium chloride, casein free from ash is deposited after some weeks in globules, which later become aggregations of needles. The small amounts of crystals obtained precluded a thorough examination of their composition; they, however, are believed to consist of the proteid in question. It is now shown that the similar proteid vitellin prepared from egg-yolk behaves in the same way; there is a considerable amount of amorphous admixture, but as in the case of casein, the thorough examination of the crystals has still to be made.

W. D. H.

Albumoses. By HUGO SCHRÖTTER (*Monatsh.*, 1898, 19, 211—222).—The two albumoses of Witte's peptone, which differ in the amounts of sulphur they contain, are only imperfectly separated by means of the hydrochlorides, acetyl, and benzoyl derivatives. With a view to obtain derivatives which might facilitate the separation, the author has studied the action of nitrous acid on this peptone. An aqueous solution containing equal weights of Witte's peptone and sodium nitrite, acidified with dilute sulphuric acid, evolves nitrogen and nitrous oxides, and deposits a pale yellow substance which is dissolved by alkalis and decomposes carbonates. The new *acid* is soluble in 60 per cent. alcohol, and crystallises from this solvent on cooling, but when boiled for a long time with dilute alcohol, it becomes insoluble,

although if then dissolved by an alkali and reprecipitated by an acid, its original solubility is regained. Analysis of the acid gave results which correspond closely with the formula $C_{108}H_{140}N_{28}O_{43}S$; its barium salt, which separates from an aqueous solution on the addition of alcohol, has the formula $C_{108}H_{136}N_{28}O_{43}SBa_2$. In many of its properties, the acid resembles the "oxyprotosulphonic acid" obtained by Maly on oxidising unpeptonised egg-albumin with potassium permanganate (Abstr., 1885, 824), but the two are not identical. The author is unable to obtain an insoluble acid by the oxidation of Witte's peptone; moreover, by further oxidation of oxyprotosulphonic acid, Maly produced peroxyprotoic acid (Abstr., 1888, 1120), which is not formed by oxidising the author's acid. The latter substance is derived from the albumose containing the higher percentage of sulphur; it gives no nitroso-reaction, and differs therein from the acid obtained by Paal from peptone hydrochloride and silver nitrite, which is a true nitroso-compound. On the other hand, the new acid resembles Schiff's desamidoalbumin in giving neither the biuret nor the nitroso-reactions, and differs from it in decomposing carbonates. The author, in reply to some observations by Fränkel and Pick, justifies his definition of albumoses as products of the transformation of egg-albumin which, besides possessing reactions in common with peptones, also contain sulphur (compare this vol., i, 502). G. T. M.

Antipeptone. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1898, 25, 195—201).—Antipeptone was separated by Kühne from the products of pancreatic digestion by means of such reagents as ammonium sulphate and trichloroacetic acid, which would free it from the amido-acids leucine and tyrosine, but not from the hexone bases, which might be formed during digestion. Hedin has previously shown that lysine is formed by tryptic activity; the present research shows that lysine, histidine, and arginine are contained mixed with the antipeptone as prepared from fibrin by Kühne, Chittenden, and Neumeister.

W. D. H.

Histon in the Urine. By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1898, 25, 236—241).—True peptone does not occur in urine; albumosuria is a more correct term than peptonuria. The difficulty of detecting this substance is increased by the fact that urobilin is precipitable by ammonia sulphate, and gives the biuret reaction. The author has previously shown that, in some of these cases, the proteid present is histon, which, although it is peptone-like, differs from other proteids in being precipitable from acid solutions by ammonia; it is also coagulable by heat. The cases are of pyogenic origin. The urine is freed from albumin and acidified with acetic acid; barium chloride is then added until no further precipitation takes place, this precipitate is collected, and after it has been allowed to remain several hours in contact with 1 per cent. hydrochloric acid, solid sodium carbonate is added until litmus paper is turned blue, and the liquid is filtered. The filtrate is then divided into two parts; with one portion the biuret reaction is performed, the other is acidified with dilute hydrochloric acid, and ammonia added; a precipitate indicates histon.

W. D. H.

Iodothyrim. By ERNST ROOS (*Zeit. physiol. Chem.*, 1898, 25, 242—251).—Baumann and others showed that the administration of iodine or iodine compounds increased the amount of iodine in the thyroid. The question whether the same can be done with the gland after removal from the body has hitherto remained unanswered. Potassium iodide and iodic acid were digested with thyroid gland and with iodothyrim. By this means, substances containing a large amount of iodine were obtained. These materials, however, are physiologically inactive. The method of artificial iodising therefore is quite a different one from that which leads to the formation of iodine compounds in the thyroid during life. W. D. H.

Presence of Emulsin in Lichens. By HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 7, 577—580).—The following lichens have been found to contain emulsin: *Cladonia pyxidata* (Ach.), *Evernia furfuracea* (Ach.), *Parmelia caperata* (D. C.), *Peltigera canina* (Ach.), *Pertusaria amara* (Nyl.), *Physcia ciliaris* (D. C.), *Ramalina fastigiata* (Pers.), *R. fraxinea* (L.), and *Usnea barbata* (L.). The enzyme was detected by placing a given quantity of the pounded lichen in contact with a solution of 0.2 gram of amygdalin in 20 c.c. of water saturated with thymol. After being kept at 35° overnight, a portion of the liquid was distilled, and the distillate tested for hydrogen cyanide. J. J. S.

Action of Pepsin and Trypsin on Protamines. By ALBRECHT KOSSEL and ALBERT MATHEWS (*Zeit. physiol. Chem.*, 1898, 25, 190—194).—Protamines (salmin and sturin) are not altered by pepsin, but they are attacked by trypsin. After the action of trypsin, protamine loses its power of precipitating albumin, and gives a red instead of a violet reaction with copper sulphate and sodium hydroxide. The substances into which protamine is changed are called protones; these are, by the prolonged action of pancreatic juice, partially broken up into hexones (lysine, histidine, arginine). There also appear to be substances intermediate between protones and hexones. The analogy between the action of trypsin on protamines (regarding them as simple proteids), and that of diastase on starch is pointed out. The fact that so large a quantity of protone resists decomposition into hexones points to the existence of an anti-group in Kühne's sense. W. D. H.

Production of Mucin by a Fluorescent Pathogenic Bacterium. By CHARLES LEPIERRE (*Compt. rend.*, 1898, 126, 761—762).—The author's previous researches have shown that a certain fluorescent bacillus produces considerable quantities of mucin when it grows in peptone culture fluids without beef. In presence of lactates, malonates, malates, tartronates, isosuccinates, pyrotartrates, ethylmalonates, glycerates, or glycollates, the mucin is produced without any fluorescence, whereas with citrates, succinates, hydroxyglutarates, hydroxypyrotartrates, and glutarates, both mucin and the fluorescent product are formed. The mucin also forms in presence of asparagine. It contains no phosphorus, and with acids yields a reducing sugar; it is, therefore, a true mucin.

The formation of mucinoid substances has also been observed in the culture-fluids of a bacillus which the authors have described as the pathogenic organism in "sleeping sickness." C. H. B.

Organic Chemistry.

A Crystalline Compound of Acetylene with Cuprous Chloride. By R. CHAVASTELON (*Compt. rend.*, 1898, 126, 1810—1812).—When cuprous acetylide is treated with hydrochloric acid in the cold, there is no appreciable evolution of gas, a fact which is attributed to the formation of a compound of acetylene with cuprous chloride, which is decomposed on warming. This compound, which analysis shows to have the composition C_2H_2, Cu_2Cl_2 , may be prepared (1) by passing acetylene into a saturated solution of cuprous chloride in dilute hydrochloric acid ($HCl + 10H_2O$ to $HCl + 7H_2O$) maintained at a temperature not exceeding 12° ; (2) by the action of acetylene on an aqueous or alcoholic solution of cupric chloride (20—40 per cent.) in presence of metallic copper. By the first, and most suitable, method, the substance is obtained in the form of large, hexagonal prisms belonging to the orthorhombic system, and by the second in silky needles, which are liable to contamination by a violet-purple deposit which is produced at the commencement of the reaction. In order to isolate the crystals unchanged, they must be quickly washed with absolute alcohol and anhydrous ether, both of these liquids having been previously cooled to 0° and saturated with acetylene, and finally dried in a current of acetylene. The crystals soon alter by exposure to air, and are immediately decomposed by water, or solutions of alkali chlorides, with evolution of acetylene and production of the violet-purple substance above mentioned, the nature of which is being investigated. On warming, they dissociate without explosion, and the following measurements of the pressure at different temperatures were made.

Temperature.	Pressure.	Temperature.	Pressure.
0°	3 mm.	46°	220 mm.
20	25 „	60	480 „
30	50 „	78	2620 „
40	131 „		

The compound described above is different from that prepared by Hofmann and Küssert (*Abstr.*, 1897, i, 546), which the author was unable to obtain. N. L.

Action of Chlorine on Ethylenic Chloride in Presence of Aluminium Chloride. Chlorination of Acetylene. By A. MOUNEYRAT (*Compt. rend.*, 1898, 126, 1805—1808).—When a mixture of dry ethylenic chloride with anhydrous powdered aluminium chloride is heated in a reflux apparatus at 70 — 75° , there is an abundant evolution of hydrogen chloride and acetylene. On passing dry chlorine into the heated mixture as long as the gas is absorbed, and subsequently pouring the liquid into hydrochloric acid, a blackish oil is

obtained which, on fractional distillation, yields some unaltered ethylenic chloride, unsymmetrical tetrachlorethane, and acetylene tetrachloride, the last-named being evidently formed by the action of chlorine on the acetylene first produced. Since, however, acetylene and chlorine unite with explosive violence under ordinary conditions, whilst no explosion took place in the experiment described, some further explanation of the reaction appeared to be necessary. In order to furnish this, a number of experiments were made, which showed that the explosion usually occurring is due to the presence of oxygen. In the absence of oxygen, chlorine and acetylene unite without explosion to form acetylene tetrachloride.

The chlorinating action of aluminium chloride appears to depend rather on the temperature at which the reaction takes place than on the amount of the reagent employed. Thus, for example, when chlorine is passed into a mixture of acetylene tetrachloride with aluminium chloride at 100°, the halogen is scarcely, if at all, absorbed; at 118—120°, however, it is rapidly absorbed, and hexachlorethane is formed. If acetylene tetrachloride is treated with bromine at 105° in presence of aluminium chloride, dichlorodibromethane, $\text{CHClBr} \cdot \text{CHClBr}$, and trichlorotribromethane are produced. The latter probably has the constitution $\text{CCl}_2\text{Br} \cdot \text{CBr}_2\text{Cl}$.
N. L.

Formation of Methanedisulphonic Acid by the Action of Acetylene on Fuming Sulphuric Acid. By WILHELM MUTHMANN (*Ber.*, 1898, 31, 1880—1884).—When a current of dry acetylene gas is passed for $1\frac{1}{2}$ hours into commercial “80 per cent.” fuming sulphuric acid, contained in a vessel immersed in ice and water, the acid gets very hot, sulphurous and carbonic anhydrides are evolved (but no carbonic oxide), and methanedisulphonic acid is formed. The reaction probably takes place in two stages, represented by the equations (1) $\text{CH}:\text{CH} + 2\text{H}_2\text{SO}_4 = \text{CH}(\text{OH})_2 \cdot \text{CH}(\text{SO}_3\text{H})_2$;

(2) $\text{CH}(\text{OH})_2 \cdot \text{CH}(\text{SO}_3\text{H})_2 + \text{SO}_3 = \text{CH}_2(\text{SO}_3\text{H})_2 + \text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O}$. The barium salt, with $2\text{H}_2\text{O}$, is rhombic [$a:b:c = 0.8946:1:1.5962$]; the potassium [$a:b:c = 1.617:1:0.9367$; $\beta = 90^\circ 12'$] and ammonium [$a:b:c = 1.6377:1:0.96964$; $\beta = 91^\circ 42'$] salts are monoclinic, and exhibit a remarkable isomorphism with the corresponding salts of imidodisulphonic acid, $\text{NH}(\text{SO}_3\text{H})_2$.
C. F. B.

Action of Acetylene on Fuming Sulphuric Acid. By GEORG SCHROETER (*Ber.*, 1898, 31, 2189—2190. Compare Muthmann, preceding abstract).—The author claims priority over Muthmann, as he has already published a brief account of his results in Richter-Anschütz's *Lehrbuch* (1897) as follows. “Methionie acid (methane disulphonic acid) is best obtained by saturating fuming sulphuric acid with acetylene, it probably results from the decomposition of an intermediate acetaldehydedisulphonic acid.” It is now shown that the formation of methionie acid can be reduced to a minimum, in this case, the chief product is acetaldehydedisulphonic acid (disulphoacetaldehyde), $\text{CHO} \cdot \text{CH}(\text{SO}_3\text{H})_2$, together with its sulphates, for example, $\text{SO}_4\text{H} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{SO}_3\text{H})_2$, which, when decomposed with hydrochloric acid, also yields disulphoacetaldehyde.

Salts of the disulphonic acid, also the phenylhydrazone, azine, and oxime have been prepared.

When boiled with alkalis, the disulphonic acid is quantitatively decomposed into salts of methionic and formic acids.

The author cannot confirm Berthelot's statement that acetylene reacts with sulphuric acid yielding acetylenesulphuric acid which, when fused with potash, gives phenol. J. J. S.

Synthesis of Potassium Carbonylferrocyanide. By JOSEPH A. MULLER (*Compt. rend.*, 1898, 126, 1421—1423).—Potassium carbonylferrocyanide, $K_3(CO)FeC_5N_5$, is readily obtained by heating a solution of potassium ferrocyanide in an atmosphere of carbonic oxide, ammonia and potassium formate being simultaneously produced. The reaction takes place rapidly at 100° , and is completed within 48 hours at 130° . A number of analyses shows that the change occurs strictly according to the equation $K_4FeC_6N_6 + CO + 2H_2O = K_3(CO)FeC_5N_5 + NH_3 + H \cdot COOK$. N. L.

Some New Ruthenocyanides and the Double Ferrocyanide of Barium and Potassium. By JAMES L. HOWE and EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, 20, 29—34).—*Strontium ruthenocyanide*, $Sr_2RuC_6N_6 + 15H_2O$, is prepared by treating lead ruthenocyanide with sulphuric acid, and then neutralising with strontium hydroxide, or, in an impure state, by the action of strontium hydroxide on "Prussian purple," the ruthenium analogue of Prussian blue; it crystallises in pale straw-coloured, elongated plates, is very efflorescent, and very soluble in water; on adding alcohol to its hot aqueous solution, it crystallises in long, slender needles.

Barium potassium ruthenocyanide, $K_2BaRuC_6N_6 + 3H_2O$, is prepared by mixing solutions of the barium and potassium salts. By the action of barium hydroxide on Prussian purple, the salt is obtained mixed with the barium salt. The pure substance crystallises from its hot aqueous solution in pale amber or colourless rhombohedra very soluble in water; crystallographically it closely resembles the corresponding ferrocyanide.

Barium caesium ruthenocyanide, $Cs_2BaRuC_6N_6 + 3H_2O$, is prepared by mixing a solution of barium ruthenocyanide with half its equivalent of caesium sulphate, when brilliant, yellowish-white to colourless crystals separate, which, under the microscope, appear to be rhombohedra, closely resembling those of the barium potassium salt; it is insoluble even in hot water, and cannot be recrystallised, as it decomposes and forms a blue insoluble substance, which is probably ruthenium cyanide.

The magnesium, sodium, and calcium salts are very soluble and difficult to crystallise; the first forms very pale green, efflorescent crystals. *Strontium potassium* and *strontium caesium ruthenocyanide* seem to resemble the barium double salts under the microscope, and not Wyruboff's potassium strontium ruthenocyanide (*Ann. chim. phys.*, [iv], 21, 279). Strontium rubidium ruthenocyanide, like strontium potassium ferrocyanide, gives a precipitate when its solution is warmed.

The authors find that potassium barium ferrocyanide prepared by

mixing solutions of the barium and potassium salts, crystallises in pale, straw-coloured rhombohedra. This salt, contrary to the statement of Wyruboff (*loc. cit.*) is perfectly stable, remaining clear and bright on prolonged exposure to air, and it crystallises, moreover, with $3\text{H}_2\text{O}$.

Barium cæsium ferrocyanide, $\text{Cs}_2\text{BaFeC}_6\text{N}_6 + 3\text{H}_2\text{O}$, obtained by decomposing barium ferrocyanide with half the equivalent of cæsium sulphate in very dilute solution, crystallises in very small, yellowish-white rhombohedra, and is sparingly soluble in water. Its hot solution appears to be stable. E. W. W.

Aliphatic Nitroso-compounds (Nitroso- and Nitro-isobutyronitrile. By OSCAR PILOTY (*Ber.*, 1898, 31, 1878—1880).—A preliminary notice. Hydroxylamidoisobutyronitrile, $\text{CMe}_2\cdot\text{C}(\text{NH}\cdot\text{OH})\cdot\text{CN}$ (von Miller and Plöchl, *Abstr.*, 1892, 1196; 1893, i, 502), can be oxidised to *nitrosoisobutyronitrile*, $\text{CMe}_2\cdot\text{C}(\text{NO})\cdot\text{CN}$, which is colourless, and melts and begins to decompose at 53° , yielding a blue liquid. If the oxidation is continued until the blue tint of the solution has disappeared, *nitroisobutyronitrile*, $\text{CMe}_2\cdot\text{C}(\text{NO}_2)\cdot\text{CN}$, is obtained; this melts at 35° , and boils at 97° under a pressure of about 45 mm.; hydrolysis with strong hydrochloric acid converts it into a substance that melts and decomposes at 110 — 112° .

The ready conversion of the $\text{NH}\cdot\text{OH}$ group into NO or NO_2 is characteristic of its presence in direct union with a *tertiary* carbon atom (this vol., i, 223). C. F. B.

Action of Charcoal in the Purification of Spirit. By MAXIMILIAN GLASENAPP (*Zeit. angew. Chem.*, 1898, 617—621; 665—672).—The author has made an exhaustive investigation as to the part which charcoal plays in the purification of spirit, and tabulated his results. The fusel oil was estimated by Rose's process, the free acids by titration with $\text{N}/20$ soda, the ethers by saponification, and the aldehydes colorimetrically by means of "rosaniline bisulphite."

From the experiments, it appears that charcoal does not absorb fusel oil, but acts chemically through the oxygen condensed in its pores. The fusel oil is oxidised to ketones and aldehydes, and the latter partially to acids, which then to some extent act on the alcohols, forming ethereal salts (compound ethers), these various mixed products causing a characteristic odour and taste. They are soluble in chloroform, and unless previously removed they would count as fusel oil in Rose's well-known process.

Charcoal absorbs these products to a large extent; in fact, filtered spirit often shows less aldehydes than the unfiltered sample. If the charcoal is afterwards heated to regenerate it, the spirit thus obtained is rich in ethers and aldehydes, but does not contain more fusel oil than the original liquor. The author advises treating the regenerated charcoal in a current of dry air so as to thoroughly impregnate it with oxygen. It is thought probable that a better product might be obtained by filtering the spirit at a somewhat higher temperature than usual. L. DE K.

Monalkyl-phosphoric Acids. By JACQUES CAVALIER (*Compt. rend.*, 1898, 126, 1285—1287).—The monethylphosphates are very

stable in solution, and are much less readily decomposed by alkalis than is the acid itself by water. In dilute solutions, there is practically no hydrolysis in presence of excess of alkali. The values obtained by the author for the heat developed by the addition of a third equivalent of a base (this vol., ii, 499) are markedly lower than the value given by Belugou (this vol., ii, 498), but agree with the corresponding value obtained by Imbert and Belugou in the case of glycerophosphoric acid. The normal salts of ethylphosphoric acid are but slightly dissociated in aqueous solution, a result which is confirmed by the sharpness of the end reaction with phenolphthalein.

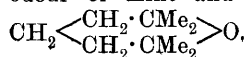
C. H. B.

Psyllostearylic Alcohol. By ERNST E. SUNDVICK (*Zeit. physiol. Chem.*, 1898, 25, 116).—A molecular weight determination by Beckmann's method, using chloroform as solvent, of the substance formerly described as psyllostearylic alcohol (Abstr., 1893, i, 125), shows that it has the formula $C_{66}H_{132}O_2$ instead of $C_{33}H_{66}O$. When heated with hydrobromic acid (sp. gr. = 1.49) during three-quarters of an hour at 210—220°, it yields a product which contains no bromine (compare *loc. cit.*), and appears to be a diatomic alcohol, $C_{33}H_{66}(OH)_2$; to this substance, the author has transferred the name *psyllostearylic alcohol*, the product formerly so named apparently being the ether, $\begin{array}{c} C_{33}H_{66}-O \\ | \\ O-C_{33}H_{66} \end{array}$.

The new substance crystallises from benzene in beautiful rhombs having an angle of 74°, and melts at 86—87° (uncorr.) after its water of crystallisation has been expelled. The latter is retained very tenaciously; the crystals obtained from light petroleum contain $13H_2O$, and after being kept 2 months in a desiccator over sulphuric acid, still retain $3H_2O$; the crystals from chloroform contain $11H_2O$, and those from benzene $10H_2O$.

W. A. D.

Dimethylheptenol, a New Unsaturated Tertiary Alcohol. By PHILIPPE BARBIER (*Compt. rend.*, 1898, 126, 1423—1426).—When lemonol (200 grams) is heated for 8 hours at 150° with potassium hydroxide (100 grams) dissolved in a little alcohol, and the product treated with water, a colourless oily liquid separates which, after rectification, boils at 79° under a pressure of 10 mm. This is shown by analysis to have the composition $C_9H_{18}O$, and since, on oxidation with chromic acid mixture, it yields methylheptenone together with small quantities of acetone and levulinic acid, it must be 2 : 6-dimethyl-2-heptene-6-ol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH$. The acetate, obtained by the action of acetic anhydride at 140°, is a liquid of agreeable aromatic odour boiling at 84—86° under a pressure of 11 mm. When dimethylheptenol is agitated for some hours with 50 per cent. sulphuric acid in the cold, it takes up a molecule of water and forms the ditertiary glycol, $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH$. The latter, being unstable, readily loses water and yields dimethylheptene oxide, a colourless, mobile liquid boiling at 132—133°, and having a strong odour of mint and camphor. It probably has the constitution



N. L.

Separation of Geraniol from Citronellol. By JULIAN FLATAU and H. LABBÉ (*Compt. rend.*, 1898, 126, 1725—1727).—The process devised by the authors for the separation of geraniol from citronellol is based upon the difference in the solubilities of the phthalates in light petroleum. The mixture of the two alcohols is boiled, in a reflux apparatus, with its own weight of phthalic anhydride dissolved in benzene, and the ethereal salts thus obtained are, after purification, dissolved in light petroleum at 20—25°. On cooling the solution to -5°, geranyl phthalate separates in the crystalline form, whilst by evaporating the remaining liquid citronellol phthalate is obtained as an uncrystallisable yellow oil. The results are given of the examination by this method of separation of a number of specimens of essence of geranium, essence of roses, &c.

Geraniol was obtained as a colourless liquid of agreeable rose-like odour, boiling at 228.2° under a pressure of 750 mm., and having a sp. gr. = 0.8965 at 0°. Citronellol boils at 221.5° under a pressure of 755 mm., and has an odour resembling both rose and geranium. *Geranyl phthalate*, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, crystallises in rhombic tablets melting at 47°, and is readily soluble in most organic solvents in the cold, with the exception of light petroleum. When treated with the theoretical amount of bromine in ethereal solution, it yields *tetrabromogeranyl phthalate*,

$\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeBr}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, which, after recrystallisation from light petroleum, melts at 114—115°. The following ethereal salts were prepared by heating citronellol or geraniol with excess of acid in sealed tubes at 150—160° in presence of anhydrous cadmium acetate; the figures represent boiling points under a pressure of 30—35 mm. *Citronellol acetate*, 172—173°; *citronellol valerate*, 194—196°; *citronellol hexoate* (from active hexoic acid), 168—170°; *citronellol crotonate*, 138—140°; *geraniol valerate*, 130—132°. N. L.

Reaction of Tertiary Alcohols and their Ethereal Salts. By GEORGES DENIGÈS (*Compt. rend.*, 1898, 126, 1277—1279).—When a tertiary alcohol is heated with an acid solution of mercuric sulphate (this vol., i, 549), it yields a more or less deep yellow or reddish precipitate identical in composition with the product obtained from the corresponding olefine under similar conditions (*loc. cit.*). Tertiary alcohols which do not yield olefines on dehydration do not give this reaction, neither do primary or secondary alcohols. On the other hand, it is obtained with the ethereal salts formed by the tertiary alcohols. In some cases, the precipitate rapidly oxidises if left in contact with the liquid in which it is formed. C. H. B.

Action of Sulphurous and Hyposulphurous Acids on Pure and Impure Solutions of Sugar. By L. BEAUDET (*Bied. Centr.*, 1898, 27, 426—427; from *Bul. Assoc. Chim.*, 15, 90).—Sulphurous acid acts very slightly on pure sugar below 50°, but acts appreciably at 55°, and very rapidly at higher temperatures. The more acid present, the greater the amount of sugar decomposed. Decomposition is much more energetic during the first 5 minutes than, for instance,

after 20 minutes. Results obtained with pure sugar do not, however, apply to syrups, &c., as even very slight amounts of impurities are sufficient to hinder the decomposition.

Hyposulphurous acid has no action either on pure or impure sugar solutions.

N. H. J. M.

Maltose. By JAMES O'SULLIVAN (*J. Soc. Chem. Ind.*, 1897, 16, 112).—Carefully purified, anhydrous maltose, prepared by acting on starch with diastase precipitated from malt extract by alcohol, has a specific rotatory power $[\alpha]_D = 155.15$, and a cupric-reducing power $K = 63$. In determining the latter, C. O'Sullivan's method (this Journal, 1876, ii, 130) was closely followed; allowance, however, should be made, in using this method, for the cupric oxide present in the ash of the filter paper, due to the absorption of the copper solution by the cellulose during filtration; in many cases, the weight of the ash is more than doubled from this cause.

W. A. D.

[NOTE BY ABTRACTOR.—Brown, Morris and Millar (*Trans.*, 1897, 100 and 110) have given for maltose the values $[\alpha]_D = 153.25$ for solutions up to 20 per cent. concentration, and $K = 62.24$].

The Carbohydrate obtained from Egg-Albumin. By OTTO WEISS (*Centralb. Physiol.*, 1898, 12, 515—516).—The carbohydrate obtained by Pavy's method from egg-albumin (freed from ovo-mucoid) is a methylpentose, and therefore an isomeride of rhamnose ($C_6H_{12}O_5$); the pentose itself crystallises in monoclinic, colourless crystals melting at 91—93°, and is soluble in water and in alcohol.

W. D. H.

A New Carbohydrate in the Liver. By JOSEF SEEGEN (*Centralb. Physiol.*, 1898, 12, 505—515).—By extracting the liver with water, a new carbohydrate, in addition to sugar and glycogen, is obtained. It does not reduce Fehling's solution, but by prolonged heating with dilute mineral acid in a closed tube, is converted into glucose. It requires 90 per cent. of alcohol to precipitate it. By treating the liver according to the Külz-Brücke method, alcohol precipitates only a small quantity of this new substance with the glycogen.

The new substance, for which the name *liver-dextrin* is suggested, is contained in the liver in quite large quantities.

W. D. H.

Nitration of Cellulose, Hydrocellulose, and Oxycellulose. By LÉO VIGNON (*Compt. rend.*, 1898, 126, 1658—1661).—Repeated treatment of cellulose, hydrocellulose, and oxycellulose with a mixture of sulphuric and nitric acids at 10—12°, together with successive analyses of the compounds produced, showed that the final product of the reaction corresponded, in each case, with the fixation of 11 NO_2 groups by a molecule containing 24 atoms of carbon. On exposure to air, nitrohydrocellulose becomes yellow and decomposes; nitro-oxycellulose is rather more stable, whilst nitrocellulose is unaffected. The behaviour of these nitro-derivatives with Schiff's reagent, Fehling's solution, and potash show that all three possess aldehydic characters, which are most marked in the case of nitro-oxycellulose. The latter also, when distilled with hydrochloric acid, yields a larger proportion of furfuraldehyde than is obtained from nitrocellulose and nitrohydrocellulose.

N. L.

Formation of Furfuraldehyde from Cellulose, Oxycellulose, and Hydrocellulose. By LÉO VIGNON (*Compt. rend.*, 1898, 126, 1355—1358).—Hydrocellulose, oxycellulose, and reduced cellulose, the last-named being apparently identical with hydrocellulose, were obtained by treating carefully purified cotton wool (10 grams) and water (1000 c.c.) with, (1) 65 c.c. of hydrochloric acid of 22°, (2) 65 c.c. of hydrochloric acid and 80 grams of potassium chlorate, (3) 65 c.c. of hydrochloric acid and 50 grams of stannous chloride. From these and some other substances, the following percentage yields of furfuraldehyde were obtained. Hydrocellulose, 0·854; oxycellulose, 2·113; reduced cellulose, 0·860; starch, 0·800; bleached cotton, 1·800; oxycellulose, prepared by means of chromic acid, 3·500. Two specimens of oxycellulose were prepared by treating cotton wool with hydrochloric acid and potassium chlorate (A), and with sulphuric acid and potassium dichromate (B), and 25 grams of each product digested with aqueous potash of 20°. Of the product A, 16·20 grams were insoluble in potash, 2·45 grams were precipitated on neutralisation of the alkaline solution, and 6·35 grams remained in solution, whilst B yielded 11·16 grams of insoluble matter, 1·42 grams were precipitated by acid, and 12·42 grams remained in solution. The percentage yields of furfuraldehyde obtained from these fractions were as follows. A, insoluble, 0·86; precipitated, 4·35; dissolved, 1·10; B, insoluble, 0·76; precipitated, 5·11; dissolved, 1·54. It appears, from the foregoing results, that the cellulose molecule, after oxidation, is easily decomposed by potash, the insoluble and larger portion having all the characters of the original cellulose, whilst the soluble portion is of an aldehydic nature, and contains a substance, precipitable by acids, which yields a relatively large amount of furfuraldehyde. N. L.

Alkyl Bismuth Iodides, and Bismuth Iodides of Vegetable Bases. By ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1898, 20, 96—100).—Alkylammonium iodides are capable of completely precipitating bismuth salts from solution, in the form of an orange-yellow powder; the *tetralkylammonium bismuth iodides* thus formed are slightly decomposed by water and by concentrated mineral acids, but are stable in the air at temperatures above 100°, and are not changed by treatment with potassium thiosulphate; they are sparingly soluble in ethylic and methylic alcohols, and insoluble in glacial acetic acid, ether, chloroform, and benzene. *Tetramethylammonium bismuth iodide*, $N_3Me_{11}HBi_2I_7$, crystallises from dilute hydrochloric acid.

Dragendorff's reagent gives, with pyridine salts, a dark orange-red precipitate of *pyridine bismuth iodide*, $(C_5NH_5)_3(HI)_2Bi_2I_6$, which can be crystallised from alcohol; atropine, strychnine, and brucine give *derivatives* of probably similar composition.

The author suggests constitutional formulæ as possibly representing the constitution of the above derivatives, in which iodine is assumed to be tervalent. W. A. D.

Chitosamine—Glucosamine. By ROBERT BREUER (*Ber.*, 1898, 31, 2193—2200. Compare Tiemann, *Abstr.*, 1884, 724; 1886, 329; 1894, i, 166; Fischer and Tiemann, *ibid.*, 1894, i, 167; Winterstein, 1896, i, 520).—Chitosamine hydrochloride can be freed from calcium sulphate

by dissolving it in 80 per cent. alcohol, and then pouring a hot concentrated aqueous solution of the purified compound into 10—15 times its volume of cold absolute alcohol, with constant stirring; 5 grams of this finely divided and dried hydrochloride is mixed with 60 c.c. of absolute alcohol and 2·5 grams of diethylamine, and the mixture left in a closed flask at the ordinary temperature for 24 hours, the crystals being treated a second, and, if necessary, a third, time in a similar manner, with the addition of a little chloroform, and finally washed with alcohol, chloroform, and a mixture of alcohol and ether in the order given. The free base, $C_6H_{13}NO_5$, is thus obtained as an extremely fine, crystalline powder, which can be recrystallised from boiling methylic alcohol; the yield is about 90 per cent. of the theoretical. The base is extremely readily soluble in water, yielding an alkaline solution; it is sparingly soluble in hot ethylic, or cold methylic alcohol, and is insoluble in chloroform or ether. When heated in a capillary tube, it turns brown at 105° , and decomposes at 110° . Its specific rotatory power $[\alpha]_D = +47\cdot08$, or, after remaining for 18 hours, $= +48\cdot83$; with a somewhat more dilute solution, the numbers found were 48·64 and 50·39 respectively.

In a perfectly dry state, it can be preserved over sulphuric acid for months, but, when kept in stoppered bottles, it is slowly converted into a brown mass, whilst in aqueous solution, decomposition takes place with the greatest readiness, ammonia being evolved. It is on account of the readiness with which it undergoes decomposition in the presence of water that the base has not previously been obtained in a pure form. Its aqueous solutions readily reduce alkaline, and even cold neutral, solutions of salts of the heavy metals.

The hydrobromide, $C_6H_{13}NO_5\cdot HBr$, is obtained when concentrated hydrobromic acid is added to a solution of the base in methylic alcohol. The *hydriodide*, obtained in a similar manner, crystallises in large, colourless plates, which are soluble in water, and also in methylic and ethylic alcohols; it turns brown at 135° , and decomposes at about 165° . A crystalline *sulphate* has also been obtained. The *oxalate*, $C_{14}H_{23}N_2O_{14}$, crystallises in fine needles when a concentrated aqueous solution is precipitated with alcohol and ether; it turns brown between 145° and 150° , and melts and decomposes at 153° . The corresponding *citrate* and *tartrate* have also been prepared, but no crystalline acetate. *Monacetylchitosamine* crystallises in long, colourless needles decomposing at about 190° ; it is readily soluble in water and in boiling methylic alcohol. The *oxime*, $C_6H_{14}N_2O_5$, crystallises from its solution in methylic alcohol in hard prisms, and melts at about 127° . The same oxime may be obtained when Winterstein's chitosamineoxime hydrochloride is suspended in alcohol and treated with diethylamine. The *diphenylhydrazone*, $C_{18}H_{23}N_3O_4$, can only be obtained in a crystalline form from the hydrochloride of the base under special conditions, and not from the base itself; it crystallises in long, colourless needles, is insoluble in absolute alcohol, ether, or chloroform, turns brown at 140° , and melts with decomposition at 162° . It dissolves in warm water, but undergoes decomposition at the same time. The *semicarbazone* of the *hydrochloride*, $C_7H_{17}N_4O_5Cl$, crystallises from 90 per cent. alcohol in small, colourless needles, and is

readily soluble in water, but insoluble in absolute methylic or ethylic alcohol. When heated in a capillary tube, it changes colour at 140° , and decomposes at 160 — 170° ; when treated with diethylamine, it yields the semicarbazone of the free base, $C_7H_{16}N_4O_5$, which crystallises in small needles melting and decomposing at 165° . d-Glucose semicarbazone, $C_7H_{15}N_3O_6$, crystallises in colourless needles melting and decomposing at 175° . All three carbazones, when heated in aqueous solution with benzaldehyde, yield benzylidenesemicarbazone.

J. J. S.

Choline and its Derivatives. By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1898, 24, 513—541).—Pure choline is probably a syrupy liquid which cannot be crystallised at the ordinary temperature; when exposed to the air, however, it becomes crystalline, owing to the formation of its carbonate by the absorption of carbonic anhydride.

Crystalline precipitates are produced in very dilute solutions of choline chloride by phosphomolybdic and phosphotungstic acids, and by iodine dissolved in potassium iodide; potassium bismuth iodide, potassium cadmium iodide, potassium mercury iodide, and mercuric and gold chlorides give precipitates with more concentrated solutions, whilst potassium zinc iodide, mercuric cyanide, platinum tetrachloride, and picric acid yield none. Brieger and others have stated that choline, unlike neurine, is not precipitated by tannin; the author finds, however, that in perfectly neutral solutions a precipitate is formed which is very soluble in acids and in alkalis; if a concentrated solution of choline chloride is employed, the hydrochloric acid produced in the reaction has to be neutralised with moist silver oxide before the precipitate will separate.

It appears that choline platinochloride, $(C_5H_{14}NOCl)_2PtCl_4$, is polymorphous; from hot solutions, rhombic (?) crystals are obtained, which, in time, change into monosymmetric prisms; $a:b:c = 1.1439:1:0.6826$; $\beta = 85^{\circ} 35\frac{1}{2}'$ (Vernadsky). The melting point of the platinochloride is not characteristic; different preparations of the pure salt melted at temperatures between 211° and 218° , whilst other investigators state that it melts at various temperatures between 225° and 241° . Hundsleben's statement (*J. pr. Chem.*, [ii], 28, 246) that choline platinochloride is anhydrous is confirmed (compare Babo and Hirschbrunn, *Annalen*, 84, 25; and Jahns, *Abstr.*, 1891, 94); 1 part of the salt dissolves in 5.82 parts of water at 21° . Choline chloride, when pure, is completely precipitated from its alcoholic solution by platinum tetrachloride, but only partially when impure. Choline aurochloride, like the platinochloride, melts at no definite temperature. The mercury double salt, $C_5H_{14}NOCl \cdot 6HgCl_2$, crystallises in rhombohedral aggregates, $a:c = 1:2.1986$, and melts at 249 — 251° ; at 24.5° , it dissolves in 56.6 times its weight of water.

Dilute solutions of choline can be boiled with barium hydroxide, and with sodium ethoxide, without undergoing change; no neurine is formed when a solution of choline chloride is evaporated with hydrochloric acid, although it appears to be produced by the slow spontaneous decomposition of choline solutions.

W. A. D.

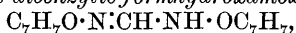
Alkyl Derivatives of Hydroxylamine. By ARTHUR R. HANTZSCH and W. HILLAND (*Ber.*, 1898, 31, 2058—2067).—By the action of methylic iodide on hydroxylamine, the authors have obtained the same product as that described by Dunstan and Goulding (*Trans.*, 1896, 839), namely, trimethylhydroxylammonium iodide, $\text{OH}\cdot\text{NMe}_3\cdot\text{I}$; for the preparation of this compound, practically the method of Dunstan and Goulding has been employed. It is readily soluble in alcohol or water, but is insoluble in ether, and gives an acid reaction, even after repeated crystallisation from alcohol. When heated, it melts and decomposes at 130° , but undergoes slow decomposition even at the ordinary temperature, and is therefore best preserved in alcoholic solution. Even when smaller quantities of methylic iodide are employed, the only product is the trimethyl derivative. *Trimethylhydroxylammonium chloride* is obtained when an aqueous solution of the iodide is digested with silver chloride until no more iodine is left in solution, the filtrate evaporated, and the residue recrystallised from hot alcohol, when the chloride is deposited as needles melting at 218° and decomposing at a slightly higher temperature. The *platinochloride*, $(\text{OH}\cdot\text{NMe}_3)_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, forms rhombohedral crystals melting and decomposing at $215\text{--}216^\circ$. The *picrate* crystallises in intensely yellow needles decomposing at $197\text{--}198^\circ$. The normal *sulphate* can only be obtained in the form of a thick syrup. The *carbonate*, obtained by digesting a solution of the sulphate with an excess of barium carbonate and evaporating the filtrate in a vacuum, crystallises from its concentrated solutions in beautiful, colourless, transparent plates. *Trimethylamine oxide* can only be obtained in aqueous solution, that is, as trimethylhydroxylammonium oxide, by carefully treating the iodide with freshly precipitated silver oxide at 0° , and then rapidly filtering from the silver iodide. The base is not soluble in ether, has a strongly alkaline reaction, rapidly absorbs carbonic anhydride, and is volatile with steam, but the greater part at the same time undergoes decomposition. Solutions of the base have strong reducing properties; silver salts, Fehling's solution, and potassium iodide solutions being immediately reduced, and in all cases a strong odour of trimethylamine is observable. The addition of alkalis to the aqueous solution also causes decomposition, and it is thus probable that trimethylhydroxylammonium hydroxide is only stable when completely ionised. Trimethylamine oxide could not be obtained by the action of nitromethane on zinc methyl.

If hydroxylamine is treated with ethylic iodide, even when a large excess of the latter is employed, the product is β -ethylhydroxylamine, and not a triethyl derivative. *β -Ethylhydroxylamine hydriodide*, $\text{OH}\cdot\text{NH}_2\text{EtI}$, crystallises in prisms, melts at 75° , is extremely hygroscopic, and readily decomposes. The chloride, platinochloride, aurochloride, and picrate could only be obtained as oils. The free base is readily decomposed. J. J. S.

Formhydroxamic Acid. By GEORG SCHROETER (*Ber.*, 1898, 31, 2190—2192).—The author cannot confirm Nef's statement (this vol., i, 102) that formhydroxamic acid, $\text{OH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, decomposes spontaneously at 0° . The acid was prepared and investigated some five years

ago by the author. A solution of pure hydroxylamine in methylic alcohol is mixed with the equivalent quantity of ethylic formate and allowed to remain for several days at the ordinary temperature; after distilling off the methylic alcohol under reduced pressure, the pure acid is obtained in colourless, glistening plates melting at $72-74^{\circ}$. It begins to decompose a few degrees above its melting point, and explodes at $80-90^{\circ}$; decomposition also takes place very slowly at the ordinary temperature, but the acid can be kept for several weeks in a desiccator. It dissolves readily in water or alcohol, but is insoluble in ether; its aqueous solution gives an intense red coloration with ferric chloride, whilst with ammoniacal copper sulphate, a green copper salt, $\text{CH} \begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ -\text{O}- \end{smallmatrix} \text{Cu}$, is obtained.

α -Benzylhydroxylamine, when heated with ethylic formate at 150° in sealed tubes, yields *dibenzyllic formhydroxamoxime*,



boiling at 170° under 15 mm. pressure. When the mixture is heated to 160° , another compound boiling at 188° under 15 mm. pressure is obtained.

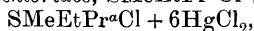
J. J. S.

Double Salts of Organic Bases with Mercury Haloids. By DANIEL STRÖMHOLM (*Ber.*, 1898, 31, 2283—2310).—Double salts of sulphinic chlorides with mercuric chloride belong to one of five classes having the general formulæ, $2\text{RCl} + \text{HgCl}_2$, $\text{RCl} + \text{HgCl}_2$, $\text{RCl} + 2\text{HgCl}_2$, $\text{RCl} + 3\text{HgCl}_2$, and $\text{RCl} + 6\text{HgCl}_2$.

The trimethylsulphine *mercurichlorides*, $2\text{SMe}_3\text{Cl} + \text{HgCl}_2$, $\text{SMe}_3\text{Cl} + \text{HgCl}_2$, $\text{SMe}_3\text{Cl} + 2\text{HgCl}_2$, and $\text{SMe}_3\text{Cl} + 6\text{HgCl}_2$, melt at 204° , 193° , 128° , and 174° respectively. Dimethylethylsulphine *mercurichloride*, $\text{SMe}_2\text{EtCl} + \text{HgCl}_2$, melts at $117-119^{\circ}$; two other double salts have been described by Klinger and Maassen. Methyl-diethylsulphine *mercurichloride*, $\text{SMeEt}_2\text{Cl} + \text{HgCl}_2$, sinters at 64° , and melts at 73° ; two other double salts have been described by Klinger and Maassen.

The triethylsulphine *mercurichlorides*, $\text{SEt}_3\text{Cl} + \text{HgCl}_2$, $\text{SEt}_3\text{Cl} + 2\text{HgCl}_2$, and $\text{SEt}_3\text{Cl} + 6\text{HgCl}_2$, melt at 82° , $126-127^{\circ}$, and $189-190^{\circ}$ respectively.

Methylethylisopropylsulphine *mercurichloride*, $\text{SMeEtPr}^i\text{Cl} + 2\text{HgCl}_2$, crystallises in elongated prisms and melts at 88.5° . The methylethyl-propylsulphine *mercurichlorides*, $\text{SMeEtPr}^n\text{Cl} + 2\text{HgCl}_2$, and



melt at $72-73^{\circ}$ and 169° respectively.

The methylethylisobutylsulphine *mercurichlorides*, $\text{SMeEt}(\text{C}_4\text{H}_9)\text{Cl} + 2\text{HgCl}_2$, $\text{SMeEt}(\text{C}_4\text{H}_9)\text{Cl} + 3\text{HgCl}_2$, and $\text{SMeEt}(\text{C}_4\text{H}_9)\text{Cl} + 6\text{HgCl}_2$, melt at $50-51^{\circ}$, 77° , and 147° respectively.

Methylethylamylsulphine *mercurichloride*, $\text{SMeEt}(\text{C}_5\text{H}_{11})\text{Cl} + 2\text{HgCl}_2$, melts at 83° .

Methyldiamylsulphine *mercurichloride*, $\text{SMe}(\text{C}_5\text{H}_{11})_2\text{Cl} + 2\text{HgCl}_2$, melts at $68-70^{\circ}$.

Methylethylhexylsulphine *mercurichloride*, $\text{SMeEt}(\text{C}_6\text{H}_{13})\text{Cl} + 3\text{HgCl}_2$, melts at $79-80^{\circ}$.

The methyldi-isobutylsulphine *mercurichlorides*, $\text{SMe}(\text{C}_4\text{H}_9)_2\text{Cl} + 2\text{HgCl}_2$ and $\text{SMe}(\text{C}_4\text{H}_9)_2\text{Cl} + 6\text{HgCl}_2$, melt at 103° and 127° respectively.

Methyldipropylsulphine *mercurichloride*, $\text{SMePr}^a_2\text{Cl} + 6\text{HgCl}_2$, melts at 121° , and methyldi-isopropylsulphine *mercurichloride*, $\text{SMePr}^s_2\text{Cl} + 6\text{HgCl}_2$, melts at 197° .

Diethylenebisulphidemethylsulphine *mercurichloride*, $\text{SMe}(\text{C}_4\text{H}_8\text{S})\text{Cl} + 3\text{HgCl}_2$, melts at 198° . Oxydiethylenebisulphidemethylsulphine *mercurichloride*, $\text{SMe}(\text{C}_4\text{H}_8\text{OS})\text{Cl} + 2\text{HgCl}_2$, has been analysed; the *mercurichloride*, $\text{SMe}(\text{C}_4\text{H}_8\text{OS})\text{Cl} + 6\text{HgCl}_2$, decomposes at 230° .

Triethylsulphine *mercuribromide*, $\text{SEt}_3\text{Br} + 6\text{HgBr}_2$, melts at 169° ; the *mercuricyanides*, $\text{SEt}_3\text{Cl} + 2\text{Hg}(\text{CN})_2$ and $\text{SEt}_3\text{CN} + 2\text{Hg}(\text{CN})_2$, melt at 100 — 101° and 158° respectively.

Methyldiethylsulphine *mercuricyanide*, $\text{SMeEt}_2\text{CN} + 2\text{Hg}(\text{CN})_2$, melts at 133 — 136° .

Tetrethylammonium *mercuricyanide*, $\text{NEt}_4\cdot\text{CN} + 2\text{Hg}(\text{CN})_2$, dissolves readily in water and in alcohol, and melts at a very high temperature.

The dimethylthetine *mercurichlorides*, $\text{COOH}\cdot\text{CH}_2\cdot\text{SMe}_2\text{Cl} + 2\text{HgCl}_2$ and $\text{COOH}\cdot\text{CH}_2\cdot\text{SMe}_2\text{Cl} + 6\text{HgCl}_2$, melt at 130° and 128° respectively. Methyllethylthetine *mercurichloride*, $\text{COOH}\cdot\text{CH}_2\cdot\text{SMeEtCl} + 6\text{HgCl}_2$, and diethylthetine *mercurichloride*, $\text{COOH}\cdot\text{CH}_2\cdot\text{SEt}_2\text{Cl} + 6\text{HgCl}_2$, have been also prepared.

The *mercurichlorides*, $\text{S} \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} \text{SCl}\cdot\text{CH}_2\cdot\text{COO}\cdot\text{HgCl} + 3\text{HgCl}_2$ and $\text{O}:\text{S} \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} \text{SCl}\cdot\text{CH}_2\cdot\text{COO}\cdot\text{HgCl} + 2\text{HgCl}_2$, melt at 180° and 162° respectively.

Ethylisopropylaniline *mercurichloride*, $\text{NEtPr}^s\text{PhCl} + 4\text{HgCl}_2$, melts at 137 — 140° .

The foregoing salts of the type $\text{RCl} + 6\text{HgCl}_2$ are isomorphous, and crystallise in rhombohedra.

When the double salts of organic bases and mercuric chloride are agitated with ether which is not quite dry, a portion of the inorganic constituent is eliminated. The action of ether has been studied in a large number of cases, and is described in the original paper, which also contains views regarding the constitution of the double salts in question.

M. O. F.

Action of Aluminium Chloride and of Chlorine in presence of Aluminium Chloride on Chloral. By A. MOUNEYRAT (*Compt. rend.*, 1898, 126, 1519—1522).—Combes found that when aluminium chloride and dry chloral are heated at 70° , carbon dichloride, a polymeride of chloral, and aluminium hydroxide are formed. The author finds that if the reaction takes place at 100° , the same products are obtained and also a considerable quantity of pentachlorethane. It would seem that part of the aluminium chloride acts in the same way as phosphorus pentachloride.

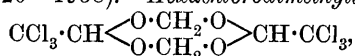
Direct experiment shows that when pentachlorethane is heated at 100° with aluminium chloride, it is quantitatively converted into carbon dichloride with liberation of hydrogen chloride, and it would follow that the latter is not a direct product of the action of aluminium chloride on chloral, but that pentachlorethane is first produced, probably with intermediate formation of a compound, $\text{AlCl}_2\cdot\text{CCl}_2\cdot\text{CCl}_3$, and is

afterwards converted into the dichloride by the further action of the aluminium chloride.

When a current of chlorine is passed into a mixture of pentachlorethane and aluminium chloride heated at 100°, hexachlorethane is obtained, the yield being quantitative. No doubt the chlorine combines with the carbon dichloride at the moment of its formation. Similarly, if bromine is dropped into the mixture of pentachlorethane and aluminium chloride, symmetrical tetrachlorodibromethane is obtained in large quantity.

C. H. B.

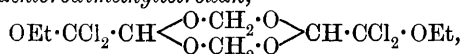
Compounds of Chloral with Formaldehyde. By ADOLF PINNER (*Ber.*, 1898, 31, 1926—1938).—*Hexachlorodimethyltetroxan*,



is prepared in the following manner. Chloral hydrate (2 parts), dissolved in a 40 per cent. solution of formaldehyde (1 part), is vigorously agitated with concentrated sulphuric acid (7 parts), and cooled meanwhile by immersing the flask in cold water; the liquid separates into two layers, and deposits crystals if shaken from time to time during 2—3 days. The solid product is collected and washed with water, being subsequently extracted with ether to remove hexachlorodimethyltrioxin. It crystallises from glacial acetic acid in highly refractive, lustrous prisms, and melts at 189°; it is insoluble in water, and dissolves with difficulty in boiling alcohol and acetone, but more readily in hot benzene and petroleum. The substance volatilises above its melting point without decomposing, the pungent odour of formaldehyde becoming perceptible; it is indifferent towards acids and alkalis at common temperatures, and nascent hydrogen eliminates only two chlorine atoms.

Tetrachlorodimethyltetroxan, $\text{CHCl}_2 \cdot \text{CH} \begin{array}{c} \text{O} \cdot \text{CH}_2 \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CH}_2 \cdot \text{O} \end{array} \text{CH} \cdot \text{CHCl}_2$, obtained on adding zinc dust to a solution of the foregoing substance in boiling glacial acetic acid, crystallises in slender, white needles, and melts at 87°.

Diethoxytetrachlorodimethyltetroxan,



is prepared by agitating hexachlorodimethyltetroxan with alcoholic sodium ethoxide in a sealed tube at 100° during 10 hours; the solution is then diluted, neutralised with carbonic anhydride, and freed from alcohol by evaporation. It crystallises from alcohol in aggregates of lustrous prisms, and melts at 114°.

Tetrachlorodimethenetetroxan, $\text{CCl}_2 \cdot \text{C} \begin{array}{c} \text{O} \cdot \text{CH}_2 \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CH}_2 \cdot \text{O} \end{array} \text{C} \cdot \text{CCl}_2$, is a by-product in the preparation of the foregoing substance, but is more conveniently obtained by heating hexachlorodimethyltetroxan (3 parts) with caustic potash (2 parts) and aniline (10—15 parts) in a reflux apparatus at 150—160° during 5—10 minutes; it crystallises in long, colourless needles or stout prisms, and melts at 106°. In preparing this compound, the alkali should be finely divided; if 2 parts of alkali to 1 part of the chloro-derivative are employed, a resinous

product containing oxalic acid is obtained, and the odour of isocyanide becomes perceptible.

Chloral methyleneglycoloxide, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{OH}$, prepared by heating hexachlorodimethyltetroxan with alcoholic ammonia at 200° , separates from the liquid in brownish prisms melting at 130° ; on submitting this compound to distillation in a current of steam, chloral methyleneglycoloxide is obtained in slender, white needles. It softens at 95° and slowly melts at 120° .

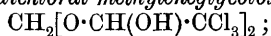
Hexachlorodimethyltrioxin, $\text{CCl}_3 \cdot \text{CH} \begin{array}{c} \text{O} \text{---} \text{CH}_2 \\ \text{O} \cdot \text{CH}(\text{CCl}_3) \end{array} \text{O}$, is obtained, as already mentioned, as a bye-product in the preparation of hexachlorodimethyltetroxan; it crystallises from alcohol in colourless, transparent, rhombic plates and melts at 129° .

Tetrachlorodimethyltrioxin, $\text{CHCl}_2 \cdot \text{CH} \begin{array}{c} \text{O} \text{---} \text{CH}_2 \\ \text{O} \cdot \text{CH}(\text{CHCl}_2) \end{array} \text{O}$, prepared by adding zinc dust to a solution of the foregoing substance in hot, glacial acetic acid, crystallises from the diluted liquid in lustrous needles melting at $67\text{--}68^\circ$; it slowly volatilises in the desiccator, giving rise to the penetrating odour of formaldehyde.

Tetrachlorodimethenetrioxin, $\text{CCl}_2 \cdot \text{C} \begin{array}{c} \text{O} \text{---} \text{CH}_2 \\ \text{O} \cdot \text{C}(\text{CCl}_2) \end{array} \text{O}$, is formed from tetrachlorodimethyltrioxin under the influence of hot alcoholic potash; it melts at $75\text{--}79^\circ$, and gradually decomposes spontaneously, yielding a fuming liquid having the odour of phosgene.

Pentachlorodimethyltrioxin, $\text{CCl}_3 \cdot \text{CH} \begin{array}{c} \text{O} \text{---} \text{CH}_2 \\ \text{O} \cdot \text{C}(\text{CCl}_2) \end{array} \text{O}$, is prepared from hexachlorodimethyltrioxin by the action of alcoholic ammonia at $150\text{--}160^\circ$, and is separated from the product by the action of a current of steam; it crystallises in colourless leaflets, and melts at $67\text{--}69^\circ$.

The resinous product obtained in the preparation of chloral methyleneglycollate is probably *dichloral methyleneglycoloxide*,



it is indifferent towards concentrated sulphuric acid at 130° , but is resolved by alcoholic potash into oxalic and glycollic acids.

M. O. F.

Production of Diacetyl from Acetaldehyde. By HANS VON RECHMANN (*Ber.*, 1898, 31, 2123—2125. Compare *Abstr.*, 1898, i, 62).—The author has already shown (*loc. cit.*) that one of the products obtained when phenylhydrazine acts on formaldehyde in acetic acid solution is glyoxalosazone. A similar reaction takes place when acetaldehyde is used, but in the case of the higher aldehydes no osazones are formed.

It is probable that the hydrazone of the aldehyde is the first product, and that this is then oxidised in the following way. $2\text{CHMe} \cdot \text{N} \cdot \text{NHPh} - \text{H}_2 = \text{NHPh} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{NHPh}$, since acetaldehyde-phenylhydrazone, when heated in acetic acid solution with phenylhydrazine, affords 10 per cent. of the theoretical amount of diacetyl-phenylhydrazone (compare Japp and Klingemann, *Trans.*, 1888, 542). The oxidation may also be accomplished by means of mercuric oxide.

If a cold solution of acetaldehydephenylhydrazone in glacial acetic acid is treated with potassium permanganate, several products are obtained. One of these is volatile in steam, and crystallises from strong hydrochloric acid in shining leaflets melting at 71° ; the mother liquor from the latter, when steam distilled, yields acetophenone and a nitrogenous substance which has not yet been characterised.

A. L.

Oxidised Cotton Oil. By WILHELM FAHRION (*Zeit. angew. Chem.*, 1898, 781—785).—See this vol., ii, 628.

Japanese Wood-oil. By JOHN H. B. JENKINS (*Analyst*, 1898, 23, 113—116).—This is an oil of high density varying from 0.9343 to 0.9385. Its viscosity at 15.5° is also very considerable, varying from 858 to 1433 secs., water in the Redwood apparatus taking 28 secs.; its drying properties exceed those of linseed oil. In applying Mauméné's heating test, it is necessary to largely dilute the sample with olive oil, as otherwise a solid mass will be obtained. Another peculiarity of this oil is that it produces a jelly with solution of iodine in chloroform or other solvents, but bromine does not cause it to solidify. Its iodine number, as determined by the Hübl method, varies from 149.7 to 165.7, but, unlike other oils, there is not the same remarkably constant ratio between the temperature rise, on treatment with bromine, and the iodine value (*Abstr.*, 1895, ii, 427), and instead of the factor 5.7, the figure 7.0 should be used.

When the oil is heated out of contact with air for a few hours at 250° , it solidifies to a sticky, elastic mass on cooling. According to Cloëz, exposure to sunlight for a few days also causes the oil to solidify. The oil has no action on polarised light, but it has a very high refractive power = 1.503 at 19° .

Although resembling linseed oil in some respects, it is plain that it contains an acid which is not one of the ordinary unsaturated type.

L. DE K.

Change Produced in Oleic Acid on Keeping. By MICHAEL VON SEŃKOWSKI (*Zeit. physiol. Chem.*, 1898, 25, 434—439).—E. Salkowski has already pointed out that when oleic acid is kept for a length of time, it is partially converted into a solid substance melting at 48° . The author has submitted this substance to closer investigation, and after determining the acid value, ether value, saponification value, iodine value, and acetyl value, concludes that it is a mixture of 32.07 per cent. of oleic acid, 8.3 per cent. of stearylactone, 20.6 per cent. of hydroxystearic acid, and 39 per cent. of some unknown substance, possibly a hydroxystearic acid, as, on analysis, it gave numbers closely agreeing with those required for such a substance.

As an explanation of this change, it is suggested that oleic acid is first converted into a lactone, according to the following equation, $C_nH_{2n+1} \cdot CH:CH \cdot C_{n+2n} \cdot COOH = C_nH_{2n+1} \cdot CH_2 \cdot CH < \underset{O}{\overset{C_nH_{2n}}{\curvearrowright}}} \cdot CO$, and that the lactone then takes up water with formation of hydroxystearic acid.

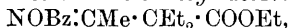
A. W. C.

Tautomerism of Ethylic Acetoacetate. By KARL SCHAUM (*Ber.*, 1898, 31, 1964—1967).—The author maintains that the addition of a substance such as sodium ethoxide or pyridine to ethylic acetoacetate cannot, as stated by Schiff (this vol., i, 355), alter the state of equilibrium between the ketonic and the enolic forms of the compound, but can only alter the rate at which the equilibrium between these forms is attained. The addition of either of these substances in small amount is found to produce no alteration in the density or index of refraction of the compound, whereas the refraction of the two forms should differ considerably. That some change does take place when the freshly distilled compound is allowed to remain, is shown by the fact that the density gradually increases for some hours after distillation.

The author is unable to account for the transformation of the compounds of ethylic acetoacetate with benzyldieneaniline by small amounts of sodium ethoxide or pyridine as described by Schiff.

A. H.

The Oxime of Ethylic Diethylacetoacetate. By MARIO BETTI (*Gazzetta*, 1898, 28, i, 274—276).—The oxime of ethylic diethylacetoacetate, $\text{NOH}\cdot\text{CMe}\cdot\text{CEt}_2\cdot\text{COOEt}$, obtained by heating the ethylic salt with hydroxylamine hydrochloride, sodium carbonate, and absolute alcohol on the water bath, forms in beautiful, colourless crystals melting at $56\text{--}57^\circ$, and is not a mobile liquid, as was stated by Westenberger (*Abstr.*, 1884, 581). It forms a crystalline sodio-derivative with sodium ethoxide, and is precipitated unaltered from the solution by hydrochloric acid; the oxime is soluble in fuming hydrochloric acid or concentrated sulphuric acid, and is precipitated unchanged on adding water. The *benzoyl* derivative,



prepared with benzoic chloride and soda, crystallises in white needles melting at $70\text{--}71^\circ$.

W. J. P.

ω -Dimethyllevulinic Acid or δ -Dimethyllevulinic (2-Methylhexan-3-onoic) Acid. By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1898, 31, 2311—2312).— ω -Dimethyllevulinic acid (*Abstr.*, 1897, i, 247), produced by oxidising β -tanacetogendicarboxylic acid, is identical with δ -dimethyllevulinic acid prepared by Fittig and Silberstein (*Abstr.*, 1895, i, 207; compare also Fittig and Wolff, *Abstr.*, 1896, i, 136). The *oxime* separates from hot benzene in lustrous crystals, and melts at $88\text{--}89^\circ$; it yields a *silver* salt, which dissolves sparingly in boiling water.

M. O. F.

Derivatives of Ethylmalonic Acid. By L. T. C. SCHEY (*Rec. Trav. Chim.*, 1897, 16, 356—360).—The ethylic salts of malonic, ethylmalonic, and diethylmalonic acids were separated by Romburgh's method (*Rec. Trav. Chim.*, 1887, 5, 235).

Ethylmalonomethylamide, $\text{CHEt}(\text{CO}\cdot\text{NHMe})_2$, was obtained by adding ethylic ethylmalonate to twice the requisite quantity of methylamine hydrochloride, and pouring this mixture into 5N potassium hydroxide, the mixture being kept for three days in a well-stoppered flask, which was shaken at intervals. The excess of the amine was then neutralised with hydrochloric acid, and the dimethyl-

amide crystallised first from benzene and then from chloroform. The yield was about 80 per cent. of the theoretical. The amide is sparingly soluble in ether or light petroleum, easily in alcohol, water, chloroform, or benzene, but does not readily crystallise from these solvents. Its melting point is 177° .

The *dimethylamide*, $\text{CHEt}(\text{CO}\cdot\text{NMe}_2)_2$, was obtained by passing a current of dimethylamine through an ethereal solution of ethylmalonic chloride. On evaporating the ether, tetramethylamide is obtained in crystals melting at 76.5° ; it is only sparingly soluble in light petroleum, but dissolves readily in other solvents. J. J. S.

Formation of Anhydrides of Aliphatic Dicarboxylic Acids. By KARL AUWERS (*Ber.*, 31, 1898, 2112—2113).—Blanc (*Bull. Soc. Chim.*, 1898, [ii], 19, 285) has laid much stress on the observation of Oddo and Manuelli (*Abstr.*, 1897, i, 180) that camphoric acid, like succinic acid and unlike glutaric acid, readily yields its anhydride when treated in dilute alkaline solution with acetic anhydride. The author finds, however, that no importance can be attached to this fact, as aaa_1 -trimethylglutaric acid and maleinoid aa_1 -dimethylglutaric acid at once afford anhydrides when subjected to this treatment. The fumaroid form of aa_1 -dimethylglutaric acid, however, is not altered when treated in this way, and in this respect resembles isocamphoric acid.

Investigation of succinic acid and its methyl-substitution derivatives has shown that an increase in the number of methyl groups in the molecule facilitates the formation of anhydride. A. L.

α -Ethylideneglutaric Acid. By FRITZ FICHTER and AUGUST EGGERT (*Ber.*, 1898, 31, 1998—2001; *Abstr.*, 1897, i, 13).— α -Ethylideneglutaric acid is the name given to the acid produced by intramolecular change during the distillation of δ -caprolactone- γ -carboxylic acid, and the authors adduce further evidence in support of the constitution, $\text{CHMe}\cdot\text{C}(\text{COOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$. The *silver, barium, and acid* and *normal calcium* salts have been prepared. The acid can also be obtained by treating the ethylic salt of the above lactonic acid with sodium ethoxide, and subsequently hydrolysing the sodium ethylic α -ethylideneglutarate thus produced. These reactions show that α -ethylideneglutaric acid stands in the same relation to δ -caprolactone- γ -carboxylic acid that the substituted itaconic acids do to the corresponding paraconic acids. When α -ethylideneglutaric acid is distilled, or treated with acetic chloride, an *anhydride* is produced which crystallises from ether and petroleum in needles melting at 87° ; sodium amalgam reduces the acid to α -ethylglutaric acid (*Abstr.*, 1896, i, 642).

The hydrogen bromide additive compound, which crystallises from petroleum in hemispherical aggregates melting at 88 — 89° , must have the constitution $\text{CHMeBr}\cdot\text{CH}(\text{COOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, since on boiling with water it yields $\gamma\delta$ -hexenoic acid, hydrogen bromide, and carbonic anhydride, and this reaction is characteristic of the hydrobromide compounds of $\alpha\beta$ -unsaturated acids containing bromine in the β -position.

$\gamma\delta$ -Dibromomethylglutaric acid, formed on adding bromine to α -ethylideneglutaric acid, crystallises from chloroform in lustrous needles,

and melts at 157—160°; when boiled with water, it decomposes into γ -bromo- γ -hexenoic acid, hydrogen bromide, and carbonic anhydride. α -Ethylideneglutaric acid, when boiled with caustic soda, is converted into an isomeride, which crystallises from benzene or chloroform in small needles, melting at 97—98°. It yields the same hydrogen bromide additive compound as the original acid, but forms a different dibromide; accordingly, the authors suppose the new acid to be α -vinylglutaric acid, $\text{CH}_3\cdot\text{CH}\cdot\text{CH}(\text{COOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, produced by a shifting of the double linking from the $\alpha\beta$ - to the $\beta\gamma$ -position.

G. T. M.

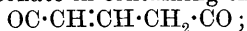
Synthesis of Symmetrical β -Hydroxytetramethylglutaric Acid. By EDMOND E. BLAISE (*Compt. rend.*, 1898, 126, 1808—1810).—Reformatsky has shown that ethylic formate interacts with two molecules of ethylic α -bromopropionate in presence of metallic zinc to form *aa*-dimethyl- β -hydroxyglutaric acid, and, in accordance with this reaction, it was expected that the action of ethylic formate on a mixture of ethylic bromisobutyrate and bromacetate would give rise to unsymmetrical β -hydroxydimethylglutaric acid. In reality, however, the ethylic formate interacts with two molecules of the ethylic bromisobutyrate to form *symmetrical ethylic β -hydroxytetramethylglutarate*, and also with the ethylic bromacetate to form ethylic propan-1-al-3-oate, $\text{CHO}\cdot\text{CH}_2\cdot\text{COOEt}$, which immediately condenses to ethylic trimesate, with elimination of $3\text{H}_2\text{O}$. At the same time, the ethylic formate reacts with 1 mol. of ethylic bromisobutyrate to form small quantities of a substance of aldehydic nature, probably of the formula $\text{CHO}\cdot\text{CMe}_2\cdot\text{COOEt}$; this could not be isolated.

Symmetrical ethylic β -hydroxytetramethylglutarate yields, on hydrolysis, the corresponding *acid*, which crystallises with difficulty from a mixture of benzene and ethylic acetate, and melts at 169—170°. When treated with acetic chloride, it yields the *anhydride* of the corresponding acetyl derivative, which crystallises in prisms melting at 90°. This anhydride is converted by the action of aniline into a *phenylamide*, crystallising in needles melting at 157°; it loses water on heating, and forms a *phenylimide*, which melts at 178°. Acetoxytetramethylglutaric anhydride, when boiled with water, yields an *acid* which readily crystallises in prisms melting at 171°. When β -hydroxytetramethylglutaric acid is heated at 135° with hydriodic acid, it is reduced to *symmetrical tetramethylglutaric acid* which melts at 113°.

N. L.

Acidic Character of Unsaturated Organic Radicles. By FERDINAND HENRICH (*Ber.*, 1898, 31, 2103—2105).—The reactivity of the methylene group in ethylic acetoacetate is attributed to its attachment to two acidic radicles. In diethylic glutaconate, the methylene group, although attached to only one acidic radicle, namely, carbonyl, is also joined to an unsaturated residue, $\text{CH}=\text{CH}$, and it still possesses the power of acting very readily, so that with methylic iodide and sodium ethoxide both mono- and dimethylglutaconic acids are obtained. The unsaturated radicle appears, therefore, to play the same part as the acidic carbonyl group.

Resorcinol is known to yield derivatives corresponding with its ketonic form (Abstr., 1887, 809, and 1888, 263), and this form resembles diethylic glutaconate in containing the grouping



it also contains another methylene group attached to the two carbonyl groups. If the author's view be correct, resorcinol should be capable of yielding tetralkyl derivatives. Herzig and Zeisel (Abstr., 1890, 1404) obtained a tetrethylresorcinol to which they gave the constitution

$\begin{array}{c} \text{HC}\cdot\text{CO}-\text{CEt}_2 \\ | \quad | \\ \text{HC}\cdot\text{CEt}\cdot\text{C}\cdot\text{OEt} \end{array}$, since it lost one ethyl group on treatment

with hydriodic acid. The formation of such a substance is most readily explained if it is supposed that the triethyl derivative which

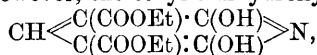
is first produced changes from the form $\begin{array}{c} \text{HC}\cdot\text{CO}-\text{CEt}_2 \\ | \quad | \\ \text{HC}\cdot\text{CHEt}\cdot\text{C}\cdot\text{OEt} \end{array}$ to the

form $\begin{array}{c} \text{HC}\cdot\text{CO}\cdot\text{CEt}_2 \\ | \quad | \\ \text{HC}\cdot\text{CH}\cdot\text{C}\cdot\text{OEt} \end{array}$, which, on further ethylation, yields the tetrethyl compound.

These results lead to the expectation that a methylene group attached to an unsaturated radicle and also to a carbonyl group will generally react like a methylene group attached to two of these acid groups. Resorcinol in its ketonic form contains two such methylene groups, and when acted on by nitrous acid forms di-isonitrosoresorcinol, just as ethylic acetoacetate yields an isonitroso-compound when similarly treated. Phenol yields quinonemonoxime with nitrous acid,

probably because its ketonic form, $\begin{array}{c} \text{CH}\cdot\text{CO}-\text{CH} \\ | \quad | \\ \text{CH}\cdot\text{CH}_2\cdot\text{CH} \end{array}$, contains a methylene group attached to two unsaturated radicles. G. T. M.

Derivatives of Glutaconic Acid. By GEORGIO ERRERA (*Gazzetta*, 1898, 28, i, 268—274).—Claisen's ethylic ethoxymethylenemalonate (Abstr., 1897, i, 592) reacts readily with ethylic sodiocyanacetate in absolute alcoholic solution, yielding the substance which the author previously considered to be diethylic α -cyanocarboxyglutaconate (this vol., i, 297); it is, however, the ethylic dihydroxynicotinate,



described by Guthzeit (Abstr., 1894, i, 71). When heated rapidly, it melts at 199°. W. J. P.

Racemic Decomposition of Rubidium Racemate. By JACOBUS H. VAN'T HOFF and WOLF MÜLLER (*Ber.*, 1898, 31, 2206—2212).—The authors have investigated Traube's rubidium racemate crystallising with 2H₂O, and have compared it with Wyruboff's anhydrous form of the twinned tartrates.

According to Traube, the decomposition of the crystallised racemate into the anhydrous tartrates should be accompanied by a partial fusion; small experiments have shown that this occurs at temperatures between 40° and 50°. Experiments with the dilatometer gave no decisive results, as the change in volume on conversion is so small; further experiments were made by the aid of a thermometer. This is the first time racemic decomposition has been studied in this way,

and the maximum of four experiments gave 40—41° (corr.). 23·5 grams of the salt was heated with a little water, and the solution stirred with a Beckmann thermometer divided in 1/100ths of a degree. The air jacket around the vessel was in a thermostat provided with an Ostwald's calcium chloride regulator, by which means the temperature was kept at about 39°, and did not vary 0·1 degree. A racemic crystal was added, and the rise in temperature observed; a fresh crystal was then added, and the maximum temperature again read, and the operation repeated until a constant maximum was obtained. That the conversion was really a racemic one, that is, was a conversion into *d*- and *l*-tartrates, was proved by adding an excess of *d*-tartrate, this was found to have no effect on the temperature of conversion. (Compare Löwenherz, Abstr., 1896, ii, 149; van't Hoff and Dawson, this vol., i, 299). The authors have determined the solubilities—(1) of the racemate; (2) of the mixed tartrates; (3) of a mixture of racemate and *d*-tartrate, and (4) of the single tartrates. The solubilities were determined by the aid of a Kenrick's apparatus, and the determination of the tartrate in presence of the racemate was made polarimetrically by Kenrick's method (Abstr., 1897, i, 506), ammonium molybdate being added in order to increase the rotation.

The results are given in the form of curves, and also of a space model. J. J. S.

Malonic Methylanilide. By DANIEL VORLÄNDER and PAUL HERMANN (*Ber.*, 1898, 31, 1826—1828).—Malonic methylanilide $\text{CH}_2(\text{CO}\cdot\text{NMePh})_2$, was prepared by heating malonamide with methyl aniline, first at 200°, and finally to 240°, distilling over the unchanged methylaniline with steam, and purifying the residue either by crystallisation from an ethereal solution, or by fractional precipitation of this solution with light petroleum. When it is dissolved in benzene and treated with sodium, hydrogen is evolved, and when a benzene solution of iodine is added to this, the liquid filtered from sodium iodide yields *ethanetetra-carboxylic methylanilide*, $\text{C}_2\text{H}_2(\text{CO}\cdot\text{NMePh})_4$; this melts at 231°, and yields succinic acid when it is boiled with hydrochloric acid. At the same time, in company with the precipitated sodium iodide, there is formed a small quantity of a substance that melts and decomposes at 164°, and is apparently *iodomalonic methylanilide*, $\text{CHI}(\text{CO}\cdot\text{NMePh})_2$; this substance is even the main product when the iodine, in absolute alcoholic solution, is added rapidly.

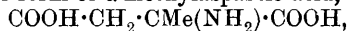
When an absolute alcoholic solution of sodiomalonic methylanilide is heated for 6 hours on a water bath with ethylic cinnamate, and the whole then allowed to remain for 20 days with excess of aqueous potash, methylaniline is formed, and dilute sulphuric acid precipitates an oil from which, after hydrolysing it with hydrochloric acid, cinnamic and β -phenylglutaric acids can be isolated (the *methylic* salt of the latter melts at 86—87°). Malonic methylanilide must thus have added itself on to ethylic cinnamate in the same way as ethylic malonate does. C. F. B.

Methylasparagine. By ARNALDO PIUTTI (*Ber.*, 1898, 31, 2039—2053).—The author has previously shown that at 105—110°,

alcoholic ammonia reacts with maleic anhydride, yielding β -asparagine (Abstr., 1897, i, 669).—Alcoholic ammonia also reacts with citraconic anhydride at 108—110°, the product being a racemic form of two enantiomorphous methylasparagines. The reaction is best carried out in a bronze autoclave; 30 c.c. of the anhydride is first introduced and then 250 c.c. of saturated alcoholic ammonia is carefully run in so that the two liquids form separate layers, a crystalline deposit being formed where the two liquids meet. After the autoclave is closed, the liquids are well mixed and then heated for 6 hours at 108—110° with constant shaking. When cold, the alcoholic liquid is removed from the solid deposit and the alcohol distilled; the residue from this is mixed with the solid deposit, dissolved in water, and converted into the *copper* derivative, $(C_5H_9N_2O_3)_2Cu + 2H_2O$, which crystallises in hexagonal lamellæ [$a : b : c = 1.96951 : 1 : 1$; $\beta = 88^\circ 06'$] of a brilliant blue colour. The methylasparagine itself is best obtained by precipitating the copper, by the aid of hydrogen sulphide, in the presence of lead carbonate; by this means, the formation of colloidal copper sulphide is avoided. Methylasparagine (glutamine), $C_5H_{10}N_2O_3 + H_2O$, crystallises from concentrated solutions in glassy, rhombic plates [$a : b : c = 1.7141 : 1 : 1.43763$], loses its water of crystallisation when exposed to the air, and when sealed in a glass tube and left for several months, gradually deliquesces. It crystallises from alcohol in an anhydrous form, turns yellow at about 240°, and melts and decomposes at 254—256°. Its solutions are optically inactive and are not precipitated by silver nitrate, by barium chloride, or by calcium chloride. Like asparagine, it combines with acids to form salts which are very readily soluble.

Methylaspartic acid (glutamic acid), $C_5H_9NO_4$, is obtained when anhydrous methylasparagine (15 grams) is boiled for 2 hours with hydrochloric acid (56.8 c.c. containing 7.821 grams of hydrogen chloride) and then treated with the requisite quantity of aqueous ammonia (28.4 c.c.). The precipitated acid thus obtained can best be purified by repeated crystallisation from boiling water; it forms crusts of small, prismatic needles, which melt and decompose at 232—234°. The crystals contain $1H_2O$, which they only lose completely when heated to 180°. The acid is insoluble in ether, and almost insoluble in absolute alcohol, but dissolves in hot dilute alcohol; it has a sweet, acid taste and is optically inactive; it forms salts with both bases and acids, the *copper* salt, $C_5H_7CuNO_4 + 4H_2O$, obtained by treating an aqueous solution of the acid with the requisite amount of copper acetate, crystallises in blue, hexagonal prisms, which are very sparingly soluble in water. When a concentrated aqueous solution of the acid is treated with nitrous acid, an acid identical with Carius's α -methylmalic acid is obtained. The author has prepared this acid by a method slightly different from that employed by Carius (*Annalen*, 1864, 129, 160) in order to compare it with his own.

Since α -methylmalic acid is the racemic form of the two enantiomorphs, $COOH \cdot CH_2 \cdot CMe(OH) \cdot COOH$, it follows that the methylaspartic acid must be the racemic form of α -methylaspartic acid,



and methylasparagine must be the racemic form of either $\text{CONH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{NH}_2) \cdot \text{COOH}$ or $\text{COOH} \cdot \text{CH}_2 \cdot \text{CMe}(\text{NH}_2) \cdot \text{CONH}_2$.
J. J. S.

“Oxymerc carbides.” By KARL A. HOFMANN (*Ber.*, 1898, 31, 1904—1909).—When sodium (10 grams) is dissolved in alcohol (150 grams) and the solution boiled (16 hours) with finely-divided yellow mercuric oxide (40 grams), the residue contains, in addition to mercury and mercury oxide, a new substance, yellow in colour but turning grey when exposed to light, which appears to have the constitution $\text{OHg}_2 \cdot \text{C}(\text{Hg} \cdot \text{OH}) \cdot \text{C}(\text{Hg} \cdot \text{OH}) \cdot \text{OHg}_2$, and is a member of a class of compounds termed by the author *oxymerc carbides*. When boiled with an aqueous solution of hydrazine, it yields nitrogen mixed with some ethane. It explodes violently at about 230° , but is not very sensitive to percussion. It is a diacid base, forming insoluble salts from which it is regenerated by treatment with alkalis; the *nitrate sulphate*, and *chloride* appear to have the constitution $\text{C}_2(\text{Hg} \cdot \text{NO}_3)_2(\text{Hg} \cdot \text{OH})_4$, $\text{C}_2(\text{Hg} \cdot \text{SO}_4\text{H})_2(\text{Hg} \cdot \text{OH})_4$, and $\text{C}_2(\text{HgCl})_6$ respectively. So firmly are the carbon and mercury united, that potassium cyanide does not separate them, but forms instead a yellow compound, $\text{C}_2\text{Hg}_2(\text{HgCN})_2$.

Paraldehyde yields the same mercarbide, and acetone and propylic alcohol form analogous ones. Methylic alcohol, however, does not form a mercarbide.
C. F. B.

Action of Mercuric Nitrate on Acetaldehyde and on Ethylic Acetoacetate. By KARL A. HOFMANN (*Ber.*, 1898, 31, 2212—2218).—Acetylene, when passed through a solution of mercuric nitrate acidified with nitric acid, yields a fine, colourless, crystalline precipitate, which, after washing with 2 per cent. nitric acid and drying under reduced pressure, has the composition $\text{C}_2\text{Hg}_2\text{NO}_4\text{H}$. (If the gas is passed through the solution for several hours, a black substance is also formed.) It is practically insoluble in water, or dilute (3 per cent.) nitric acid, but is decomposed by concentrated acid. With warm dilute hydrochloric acid, it yields acetaldehyde, and mercuric chloride goes into solution. When treated with alkalis, the nitrogen is obtained in the form of nitrates, and when warmed with sodium hydroxide and potassium cyanide solution, aldehyde resin is formed. The compound may be obtained in the form of large crystals by using an alcoholic solution of aldehyde in place of acetylene; after remaining for 14 days, large, colourless, doubly-refractive prisms, terminated by pyramids, are deposited. The constitution suggested is $\text{NO}_3 \cdot \text{Hg} \cdot \text{C}(\text{Hg}) \cdot \text{CH} \cdot \text{O}$. The author suggests that the substance obtained by Poleck and Thümmel (*Abstr.*, 1890, 118) by shaking commercial ether with an aqueous solution of mercuric chloride and potassium hydrogen carbonate, is probably a somewhat similar compound, only contaminated by a little mercurous chloride. A compound, $\text{C}_6\text{H}_8\text{HgO}_3$, may be obtained by adding ethylic acetoacetate to an acidified solution of mercuric nitrate, provided the nitrate solution is sufficiently dilute and that the temperature is kept below $+5^\circ$; it is insoluble in water, and is decomposed when warmed with dilute nitric acid, the ethereal salt being regenerated. Acetone yields a pale yellow compound, $\text{C}_3\text{Hg}_3\text{H}_5\text{O}(\text{NO}_3)_2$. It thus

appears probable that mercury is able to replace hydrogen atoms attached to a carbon atom in the α -position relatively to an aldehydic or ketonic group.

The compound $C_2Hg_2NO_4H$, when heated with an ethereal solution of ethylic iodide (two molecules for each atom of mercury), yields a yellow substance, $C_2Hg_3I_2$, which is insoluble in water, dilute nitric acid, or potassium iodide solution. On exposure to light, it rapidly turns grey. Dilute aqueous sodium hydroxide decomposes the nitrate, $C_2Hg_2NO_4H$, yielding a black residue consisting largely of metallic mercury. If this residue is extracted with 5 per cent. sodium hydroxide, then with cold dilute nitric acid, and finally with 10 per cent. hydrochloric acid, a colourless residue of the compound, $C_2Hg_6Cl_6$, is obtained (preceding abstract). The filtrate from the black residue, when neutralised with carbonic anhydride, nitric acid, or the requisite quantity of hydrochloric acid, yields in each case a white precipitate. The *nitrate*, $C_2Hg_3NO_6H$, obtained when nitric acid is employed, yields no aldehyde when treated with hydrochloric acid or with alkali and potassium cyanide. The *chloride* has the composition $C_2Hg_3Cl_3O_2H$. These salts, when treated with alkali, leave a grey residue consisting of mercury and the explosive oxymercarbide, $C_2Hg_6O_4H_2$.

J. J. S.

Occurrence of Ketopentamethylene in Wood-oil. By HERMANN METZNER and DANIEL VORLÄNDER (*Ber.*, 1898, **31**, 1885—1886).—Ketopentamethylene can be detected in the products of the dry distillation of calcium succinate; by treating the fraction boiling at 100—160° with benzaldehyde and caustic soda, dibenzylideneketopentamethylene can be isolated. Furan appears also to be contained in the product.

Ketopentamethylene is probably always formed when wood is distilled, and if it has been found in but few examples of wood-oil, this is possibly because most manufacturers pass the crude products, while still in the gaseous state, through milk of lime, which may convert the ketopentamethylene into substances of high boiling point.

C. F. B.

Stereoisomeric 1:3-Pentamethylenedicarboxylic Acids. By KARL THEODOR POSPISCHILL (*Ber.*, 1898, **31**, 1950—1957).—*Cyclopentane-1:1:3:3-tetracarboxylic acid*, $\begin{matrix} CH_2 \cdot C(COOH)_2 \\ | \\ CH_2 \cdot C(COOH)_2 \end{matrix} > CH_2$, prepared by heating ethylic butanetetracarboxylate with sodium ethoxide and methylenic iodide, and hydrolysing the ethereal salt produced, forms a white, hygroscopic, crystalline mass which melts at 186—188°, vigorously evolving carbonic anhydride; the product of this change is cyclopentane-1:3-*cis-cis*-dicarboxylic acid, which is also formed on evaporating the aqueous solution of the tetracarboxylic acid.

The *anhydride* of cyclopentane-1:3-*cis-cis*-dicarboxylic acid, $C_7H_8O_3$, obtained by heating the crude acid with acetic anhydride in a reflux apparatus, crystallises from ethylic acetate in lustrous, monoclinic plates, melts at 160—161.5°, and boils at 215—218° under a pressure of 90 mm. The *acid*, $C_7H_{10}O_4$, crystallises from water in lustrous, flattened prisms, and melts at 120—121.5°.

Cyclopentane-cis-trans-dicarboxylic acid, $C_7H_{10}O_4$, produced on heating the foregoing acid at 180° during 4 hours, crystallises from carbon tetrachloride in small, flattened prisms, and melts at $87-88.5^\circ$; prolonged treatment with boiling acetic anhydride converts it into the anhydride of the *cis-cis*-modification. The *silver* salt is obtained from both acids as an amorphous precipitate, which is extremely sensitive to light and heat, and is almost insoluble in water. The *calcium* salt of the *cis-cis*-acid crystallises in monoclinic plates, and requires five times its weight of water to dissolve it at 30° ; the *calcium* salt of the *cis-trans*-modification crystallises in nodules, and dissolves in its own weight of water; both salts contain $2\frac{1}{2}H_2O$. The *barium* salts are very readily soluble, and crystallise in slender needles; the *lead* salts are amorphous.

The *methyl*ic salt of the *cis-cis*-acid boils at $138-138.5^\circ$ under a pressure of 25 mm. The *diamide* crystallises from water in slender needles and melts at $224-226^\circ$, yielding the *di-imide*, which melts at $154-155^\circ$ and boils above 360° ; the *dianilide* crystallises from methyl alcohol in leaflets, and melts at $222-224^\circ$. M. O. F.

Cyclic Compounds. By WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1898, 301, 154-202).—This paper scarcely lends itself to condensation. After pointing out the advantages offered by Caucasian naphtha as a source of cyclic compounds, the author proceeds to the isolation of its constituents. Fractionations of some specimens of "benzin" are detailed, and the specific gravity of every fraction is recorded; from these data, curves are plotted, correlating density and boiling point. Great importance is attached to specific gravity, which is regarded as the best criterion of the state of purity in which the hydrocarbons are isolated from the mixture.

The belief that hexanaphthene yields dinitrobenzene under the influence of nitric acid is now found to be untenable. It is extremely difficult to separate benzene from cyclic hydrocarbons boiling at a much lower temperature than that substance, and, before this was realised, it was not unnatural to suppose that the dinitrobenzene obtained from the fraction boiling at $60-70^\circ$ was produced at the expense of the hexanaphthene in the mixture, the more especially as the boiling point of the latter underwent no change in the process; if, however, triphenylmethane is dissolved in the hydrocarbons, and the solution cooled, the benzene compound of triphenylmethane crystallises from the mixture, which then yields dinitrobenzene no longer.

Directions are given for preparing the chlorides, bromides, and iodides of the naphthenes, and also their nitro-, amido-, and hydroxy-derivatives; the conversion of the naphthenes into naphthylenes, and the behaviour of the former towards oxidising agents, are described, and it is pointed out that, under favourable conditions, cyclic hydrocarbons which do not contain a side chain are converted by nitric acid into dibasic acids containing the same number of carbon-atoms.

M. O. F.

Derivatives of Cycloheptane. By EDUARD BUCHNER and ANDREAS JACOBI (*Ber.*, 1898, 31, 2004-2009. Compare this vol., i, 301).—The authors call attention to the great similarity existing between

their seven-membered ring compounds derived from suberone and the so-called ethyleyclopentane derivatives, obtained by Einhorn and Willstätter from paramethylenedihydrobenzoic acid (Abstr., 1894, i, 524), and they suggest that the two series may, in reality, be identical; this view is supported by the fact that derivatives of both series are convertible into paratoluic acid.

Chlorosuberanecarboxylic acid (1-chlorocycloheptanecarboxylic acid), $C_7H_{12}Cl \cdot COOH$, obtained either by heating hydroxysuberanecarboxylic acid with hydrochloric acid, or by warming it with phosphorus pentachloride on the water bath, crystallises from weak alcohol in colourless leaflets melting at $42-44^\circ$. This acid forms the starting-point in the preparation of the suberenecarboxylic acid and its amide, and of suberanecarboxylic acid and its amide; these compounds which were only briefly alluded to in a previous communication (this vol., i, 301), are now more fully described.

Suberenecarboxylic acid dibromide (1:2-dibromocycloheptanecarboxylic acid), $C_7H_{11}Br_2 \cdot COOH$, produced by adding bromine to suberenecarboxylic acid, forms a colourless, crystalline mass which melts at 135° .

Bromosuberanecarboxylic acid (1-bromocycloheptanecarboxylic acid), $C_7H_{12}Br \cdot COOH$, prepared by treating suberanecarboxylic acid with bromine and phosphorus, crystallises from hot formic acid in colourless needles melting at $89-91^\circ$.
G. T. M.

Azelaone and Azelaol. By K. G. HANS DERLON (*Ber.*, 1898, 31, 1957—1964).—When azelaic acid or its calcium salt is distilled with lime, a small amount of *azelaone*, $C_8H_{14}O$, is formed, which distils at $80-91^\circ$ under a pressure of 22 mm. The compound with sodium hydrogen sulphite cannot be obtained pure, and the *oxime* has only been isolated in the form of an oil boiling at $140-160^\circ$ under a pressure of 100 mm. The *semicarbazone*, $C_8H_{14} \cdot N \cdot NH \cdot CO \cdot NH_2$, crystallises in colourless, lustrous prisms melting at 85° . On oxidation with potassium permanganate, this ketone yields a small amount of suberic acid, $C_8H_{14}O_4$, and this reaction proves that azelaone is the normal cyclo-octanone, $CH_2 < \begin{smallmatrix} CH_2 \cdot CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CH_2 \end{smallmatrix} > CO$. On reduction with alcohol and sodium, it is converted into the corresponding alcohol, *azelaol*, $C_{18}H_{15} \cdot OH$, which is a colourless oil boiling at $187-188^\circ$ under a pressure of 749 mm.
A. H.

Dialdehyde of Adipic Acid. By ADOLF VON BAEYER and HANS VON LIEBIG (*Ber.*, 1898, 31, 2106—2110. Compare Abstr., 1897, i, 588).—When dihydroxysebacic acid is treated with lead peroxide, the dialdehyde of suberic acid is produced; dihydroxysuberic acid, under similar conditions, yields, not the dialdehyde of adipic acid, but a condensation product of this substance.

Dihydroxysuberic acid is best prepared by heating dibromosuberic acid with barium hydroxide; the employment of caustic potash results in the formation of amorphous products.

Δ^1 -Cyclopentenealdehyde is the final product of the action of lead peroxide on dihydroxysuberic acid in the presence of acetic and phosphoric acids; it is separated from the mixture by distillation with steam, and when subsequently rectified, forms a colourless liquid with

a pungent odour resembling that of benzaldehyde. The yield obtained is very small and the substance readily decomposes; on this account, its boiling point was not determined. It is readily soluble in water, and on adding semicarbazide hydrochloride to the solution, the *semicarbazone* is obtained, crystallising from water or alcohol in hexagonal leaflets, and melting at 208°. The oxime does not crystallise, and the hydrazone forms colourless leaflets which speedily resinify.

Δ^1 -Cyclopentenecarboxylic acid (Abstr., 1893, i, 557), resulting from the oxidation of the aldehyde with silver oxide, crystallises from water in leaflets or needles and melts at 120°. The copper salt forms blue, tabular crystals which change, on heating, into a white powder; the silver salt crystallises from water in hexagonal leaflets.

α -Hydroxyvaleric acid is readily converted into isobutaldehyde on treatment with lead peroxide and phosphoric acid; the semicarbazone of this aldehyde melts at 124°. G. T. M.

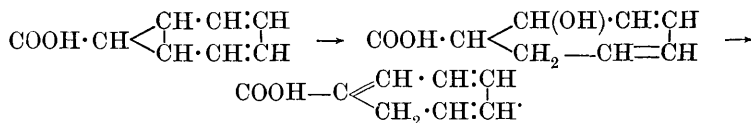
Pseudophenylacetic Acid. By EDUARD BUCHNER (*Ber.*, 1898, 31, 2241—2247).—The ethereal salt of this acid, which results from the action of ethylic diazo-acetate on benzene, is readily converted into two isomeric acids, the so-called α - and β -isophenylacetic acids (compare this vol., i, 314).

These two acids are both cycloheptatrienecarboxylic acids; they give rise to the same dihydrobromide and to a cycloheptanecarboxylic acid identical with that previously described under the name of suberane-carboxylic acid (*Trans.*, 1881, 541); furthermore, they are closely related to the so-called paramethylenedihydrobenzoic acids obtained from the coca alkaloids, and are also derivatives of cycloheptatriene. Four cycloheptatrienecarboxylic acids are theoretically possible, and four such acids have been obtained. The isomerism depends on the positions occupied by the three double linkings in the heptatriene ring, and until these have been determined with certainty in the case of each isomeride, the acids will be distinguished as α -, β -, γ - and δ -cycloheptatrienecarboxylic acids.

	Former designation.	Reference.	M.p. of acid.	M.p. of amide.
α -Acid	α -Isophenylacetic acid.	Abstr., 1897, i, 282.	71°	129°
β -Acid	p -Methylenedihydrobenzoic acid. β -Isophenylacetic acid.	Abstr., 1893, i, 538. This vol., i, 314.	55° 55	101° 98
γ -Acid	p -Methylenedihydrobenzoic acid. γ -Isophenylacetic acid.	Abstr., 1895, i, 92. Succeeding abstract.	An oil ,,	90° 94—96
δ -Acid	p -Methylenedihydrobenzoic acid.	Abstr., 1893, i, 378	32°	125·5°

The author's previous suggestion that pseudophenylacetic acid has

the constitution, $\text{COOH} \cdot \text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CH} \\ | \\ \text{CH} \cdot \text{CH} \cdot \text{CH} \end{smallmatrix}$, is in accordance with subsequent investigations; its amide, on hydrolysis with caustic soda, readily yields α -isophenylacetic acid, which is probably $\Delta^{1,3,5}$ -Cycloheptatrienecarboxylic acid; the reaction is assumed to take place in the following manner:—



When isophenylacetic acid dihydrobromide, obtained from either α - or β -isophenylacetic acid, is reduced with sodium and amyl alcohol, cycloheptanecarboxylic acid and a crystalline compound, $\text{C}_8\text{H}_{12}\text{O}_3$, are obtained; the latter is acidic, melts at $125-126^\circ$, crystallises from ether in colourless prisms, and probably has the constitution $\text{C}_7\text{H}_{11}\text{O} \cdot \text{COOH}$. Its composition was previously given as $\text{C}_6\text{H}_{10}\text{O}_2$ (Abstr., 1897, i, 283).

The above dihydrobromide, when reduced with zinc dust and alcoholic hydrogen chloride, yields *bromocycloheptenecarboxylic acid* which melts at $150-151^\circ$; its amide, $\text{C}_7\text{H}_{10}\text{Br} \cdot \text{CONH}_2$, crystallises from ether in colourless needles and melts at $134-135^\circ$.

When heated with a solution of hydrogen bromide in acetic acid, isophenylacetic acid is converted into dibromotetrahydroparatoluic acid and *tribromocycloheptanecarboxylic acid*; the latter crystallises from ether in colourless rhombohedra, melts at 199° , and is not attacked by alkaline permanganate solution. The former product is identified by conversion into paratoluic and terephthalic acids. G. T. M.

β -Isophenylacetic Acid (β -Cycloheptatrienecarboxylic Acid). By EDUARD BUCHNER and FERDINAND LINGG (*Ber.*, 1898, 31, 2247—2250. Compare preceding abstract.)—This acid, when dissolved in glacial acetic acid saturated with hydrogen bromide, forms dibromocycloheptenecarboxylic acid, $\text{C}_7\text{H}_6\text{Br}_2 \cdot \text{COOH}$, identical with that obtained from its α -isomeride. Both isomerides, on treatment with bromine in glacial acetic acid, give the same *tetrabromocycloheptenecarboxylic acid*, which crystallises from this solvent in prisms melting at $192-194^\circ$; the mother liquors from the experiment with the α -isomeride also yield a tetrabromide which melts at $176-178^\circ$, and is very probably identical with that melting at $174-175^\circ$ obtained by Einhorn and Willstätter from paramethylenedihydrobenzoic acid (Abstr., 1894, i, 524). γ -Cycloheptatrienecarboxylic acid is produced on boiling the β -acid for 48 hours with alcoholic potash; it forms an oil which, on treatment with phosphorus pentachloride and ammonia, yields an amide melting at $94-97^\circ$. Einhorn and Willstätter (*loc. cit.*) obtained the same acid from the two crystalline paramethylenedihydrobenzoic acids. G. T. M.

Chlorinating Action of Ferric Chloride in the Aromatic Series. By VICTOR THOMAS (*Compt. rend.*, 1898, 126, 1211—1214).—Ferric chloride readily chlorinates aromatic hydrocarbons, especially

on heating; hydrogen chloride is evolved, and there is much charring. The products obtained from benzene include chlorobenzene, 1:4-dichlorobenzene, 1:2:4-trichlorobenzene, 1:2:4:5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, and possibly small quantities of derivatives isomeric with these. Bromobenzene is converted by the action of ferric chloride into 1:4-chlorobromobenzene, whilst toluene yields a mixture of chlorotoluenes and derivatives richer in chlorine than these, substitution taking place only in the benzene nucleus. With benzylic chloride, there is produced a blackish resin, soluble in benzene, analogous to the substance $(\text{CH}_2\text{Ph})_n$, which Friedel obtained by the interaction of benzylic chloride and aluminium chloride.

N. L.

Action of Bromine on Phenols in Presence of Aluminium Bromide. By F. BODROUX (*Compt. rend.*, 1898, 126, 1282—1285).—The author has investigated the products obtained from phenols by the action of excess of bromine containing a small quantity of aluminium bromide. Phenol yields the pentabromophenol described by Körner; it forms long, silky needles which melt at 225°. Orthocresol, metacresol, and paracresol yield tetrabromo-derivatives which crystallise in long, white needles melting at 207—208°, 194°, and 198—199° respectively. Thymol yields tetrabromometacresol.

With polyhydric phenols, the reactions are less definite. Resorcinol yields a black, gummy mass; quinol yields some tetrabromoquinol mixed with more complex products.

Orthonitrophenol yields the 4:6:2-dibromonitrophenol melting at 117—118°, and paranitrophenol, the 2:6:4-dibromonitrophenol melting at 141°. In the case of these nitro-derivatives, the products are the same as in the absence of aluminium bromide.

C. H. B.

Action of Sulphuryl Chloride on Phenols and their Ethers. By ALBERTO PERATONER (*Gazzetta*, 1898, 28, i, 197—240).—The author discusses at length the action of sulphuryl chloride on phenols and their ethers, and applies Nef's views as to the addition of halogen and subsequent elimination of hydrogen haloid to obtain an explanation of the reactions concerned.

[With G. B. CONDORELLI.]—Parachlorophenol alone is obtained by the action of pure sulphuryl chloride on phenol, but if the chloride be impure, 2:4-dichlorophenol is simultaneously formed.

5-Chlororthocresol, obtained by the action of sulphuryl chloride on orthocresol, crystallises in colourless needles melting at 48—49°, and its benzoate, $\text{C}_{14}\text{H}_{11}\text{ClO}_2$, forms colourless, pearly laminae melting at 71—72°. The methylic ether has a pleasant odour, boils at 212.6—214.6° under 758.4 mm. pressure, and is oxidised by permanganate, yielding 5-chloromethylsalicylic acid, which crystallises in minute needles melting at 81—82°; its barium salt crystallises with $2\text{H}_2\text{O}$ in lustrous plates, and on warming the acid with hydriodic acid, it yields the 5-chlorosalicylic acid melting at 171—172.5°. Orthotolyl benzoate boils at 303—305°, and does not react with sulphuryl chloride.

6-Chlorometacresol, obtained by the action of sulphuryl chloride on metacresol, crystallises in long, colourless needles melting at 52—53°, and boils at 235.9° under a pressure of 757.7 mm.; its methylic ether

boils at 215.5—217.5° under 759 mm. pressure, and on treatment with alkaline permanganate yields 6-chloro-3-methoxybenzoic acid, $C_8H_7ClO_3$, which crystallises in colourless needles melting at 160—161°. When warmed with hydriodic acid, this acid gives 6-chloro-3-hydroxybenzoic acid, which melts at 169—170°; its constitution is determined by converting it into 4-chloro-2-nitrophenol.

Parachlorothymol, melting at 62—64°, is obtained by treating thymol with sulphuryl chloride; its constitution is evident from its yielding thymoquinone on oxidation with manganese dioxide and sulphuric acid. The *methylic* ether of parachlorothymol is a liquid boiling at 251° under 760.2 mm. pressure.

[With CARM. VITALI.]—Sulphuryl chloride reacts with parabromophenol at the ordinary temperature, giving a small quantity of parachlorophenol melting at 37° (compare Ling, Trans., 1892, 61, 560). The *benzoate* of parabromophenol melts at 102—103°, and does not react with sulphuryl chloride. Mazzara and Lamberti (Abstr., 1897, i, 182) have already shown that 3-chloro-1:4-cresol is obtained on treating paracresol with sulphuryl chloride; the *methylic* derivative, C_8H_9OCl , boils at 215—218° under 760.8 mm. pressure, and yields 3-chloranistic acid melting at 212—214° on oxidation with alkaline permanganate. *Paratolylic benzoate* melts at 141°.

Isopropylphenol reacts with sulphuryl chloride, yielding 3-chloroisopropyl-4-phenol, a liquid which boils at 230—232° under 760 mm. pressure, and does not crystallise at -18°; its *methylic* derivative, $C_{10}H_{13}ClO$, is a colourless oil of aromatic odour boiling at 246.7—248.7° under 759.4 mm. pressure, and yields 3-chloranistic acid on oxidation with permanganate.

Paracumophenol acetate boils at 238—240°, and is but slightly acted on by sulphuryl chloride. Parabenzylphenol is, however, converted into a *chlorobenzylphenol*, $C_{13}H_{11}ClO$, which boils at 318—321°, with partial decomposition, in a current of carbonic anhydride; it is not volatile in a current of steam. *Parabenzylphenol acetate* boils at 310°, and is only slightly attacked by sulphuryl chloride. Paranitrophenol and its benzoate, and also picric acid are not acted on by sulphuryl chloride.

Catechol and sulphuryl chloride react violently, but by using ether as a solvent, and cooling, a *monochlorocatechol*, $C_6H_5ClO_2$ [OH:OH:Cl = 1:2:4], is obtained; it crystallises in lustrous scales melting at 80—81°, and its *methylic* derivative is identical with the monochloroveratrole described below. The use of a larger proportion of sulphuryl chloride leads to the formation of a *dichlorocatechol*, $C_6H_4Cl_2O_2$ [OH:OH:Cl₂ = 1:2:4:5], which crystallises in colourless needles melting at 105—106°, and is converted into 1:2:4:5-tetrachlorobenzene by phosphorus pentachloride; the dichlorocatechol, on methylation, gives the dichloroguaiacol melting at 71—72°. Catechol monobenzoate is not acted on by sulphuryl chloride.

Sulphuryl chloride reacts with pyrogallol, yielding a *monochloropyrogallol*, $C_6H_5ClO_3$, melting at 143°, of which the benzoate melts at 140°, and of a *dichloropyrogallol* melting at 128°, of which the benzoate melts at 165°; the trichloropyrogallol obtained by Webster (Trans. 1884, 45, 205), and melting at 175°, is also formed.

[With G. ORTOLEVA.]—Parachloranisole and parachlorophenetole are respectively obtained by the action of sulphuryl chloride on anisole and phenetole. The methylic ethers of ortho- and para-cresol similarly yield the methylic ethers of parachlororthocresol and orthochloropara-cresol; these, on oxidation with permanganate, give 5-chloromethyl-salicylic acid melting at 81—82°, and 3-chloranisic acid melting at 213° respectively. Thymol methylic ether, on treatment with sulphuryl chloride, yields the methylic ether of parachlorothymol described above.

Monochloroguaiacol, $C_7H_7ClO_2$, is obtained as a colourless oil on treating guaiacol with sulphuryl chloride; it boils at 239—241·5° under 757·7 mm. pressure, and, on methylation, yields the monochloroveratrole described below; the *benzoate*, $C_7H_6BzClO_2$, crystallises in tiny, colourless scales melting at 76—77°. Using a larger proportion of sulphuryl chloride, a dichloroguaiacol, $C_7H_6Cl_2O_2$, which crystallises in long, colourless needles melting at 71—72°, is obtained; its *benzoate*, $C_7H_5BzCl_2O_2$, melts at 72—74°. With a yet larger proportion of sulphuryl chloride, a *trichloroguaiacol*, $C_7H_5Cl_3O_2$, crystallising in colourless needles melting at 107—108° is obtained; its *benzoate*, $C_7H_4BzCl_3O_2$, melts at 128—129°. Guaiacol acetate is not acted on by sulphuryl chloride.

With sulphuryl chloride, veratrole yields *monochloroveratrole*,

$C_8H_9ClO_2$ [OMe : OMe : Cl = 1 : 2 : 4], as a colourless oil boiling at 242·4° under 763·3 mm. pressure, and also *dichloroveratrole*, $C_8H_8Cl_2O_2$ [OMe : OMe : Cl₂ = 1 : 2 : 4 : 5], which crystallises in colourless needles melting at 85·5—86·5°.

Ortho-, meta-, and para-hydroxybenzoic, protocatechuic, thymotic, paracumophenolorthocarboxylic, benzoic, and methylsalicylic acids, and the ethylic salts of the phenolsulphonic acids, are not acted on by sulphuryl chloride; but salicylaldehyde yields the 5-chlorosalicylaldehyde melting at 98°, and parahydroxybenzaldehyde gives the 3-chloro-derivative melting at 148°. Vanillin yields a *chloro*-derivative, $C_8H_7ClO_3$, with sulphuryl chloride; this crystallises in colourless, lustrous laminae melting at 158—160°.

Ethylic phenylic carbonate, salol, and triphenylic phosphate do not react with sulphuryl chloride. Phenylic oxide yields a mixture of mono- and dichloro-derivatives which could not be separated, whilst xanthen gives a *dichloro*-derivative, $C_{13}H_8Cl_2O$, which melts at 148—149°, and apparently yields a dichloroxanthone melting at 181° on oxidation.

Phenyl benzyl ketone gives, with sulphuryl chloride, a *trichloro*-derivative boiling at 160—175°; this could not be purified, but, on heating with hydrochloric acid in a sealed tube, yields 2 : 4 : 6-trichlorophenol.

Phenoxyacetic acid is converted by sulphuryl chloride into parachlorophenylacetic acid, which crystallises in colourless needles melting at 150—151°, and, on hydrolysis with fuming hydrochloric acid, yields parachlorophenol.

W. J. P.

Alkylanisoles and Alkylphenetols. I. Orthethylphenetole. By PAUL JANNASCH and WILLY HINRICHSSEN (*Ber.*, 1898, 31, 1824).—Iodophenetole (25 grams), prepared from phenetidine by Sandmeyer's

reaction, and ethylic iodide (20 grams) were diluted with benzene, heated with sodium (8 grams) for 4—5 hours at 120—140°, and then allowed to remain for some time. The whole was then filtered, the solid residue washed with benzene, and the united filtrates distilled, the part boiling above 125° being then fractionated carefully. *Orthethylphenetol*, $C_6H_4Et \cdot OEt$, boils at 189—192°. C. F. B.

Derivatives of Ethylenecatechol [Catechol Ethylenic Ether]. By CHARLES MOUREU (*Compt. rend.*, 1898, 126, 1426—1428).—Catechol ethylenic ether is readily obtained in quantity by heating catechol with potash, ethylenic bromide, and water, in a reflux apparatus filled with hydrogen to prevent oxidation. It is an oily liquid, insoluble in water, boiling at 216° (corr.), and having a sp. gr. = 1.186 at 0°. Potassium permanganate, hydriodic acid, and ammonia have no action on it, even at high temperatures, whilst chromic acid oxidises it completely to oxalic and carbonic acids. Substitution derivatives in which the ethylene group is concerned are best obtained indirectly. Thus, by the action of dibromhydrin, $CH_2Br \cdot CHBr \cdot CH_2 \cdot OH$, on the sodium

derivative of catechol, the compound, $C_6H_4 \begin{smallmatrix} O \cdot CH_2 \\ \diagup \quad \diagdown \\ O \cdot CH \cdot CH_2 \cdot OH \end{smallmatrix}$, is obtained which crystallises in fine, colourless needles melting at 89—90° and boiling without decomposition at 283—286°. The corresponding *acetate* boils at 185—188° under a pressure of 30 mm. The sole product of the action of nitric acid on catechol ethylenic ether was found to be the mononitro-derivative, melting at 121°, which has previously been obtained by Vorländer, and appears, from the following considerations,

to have the constitution $C_6H_3(NO_2) \begin{smallmatrix} O \cdot CH_2 \\ \diagup \quad \diagdown \\ O \cdot CH_2 \end{smallmatrix} [O : O : NO_2 = 1 : 2 : 4]$.

When the sodium derivative of protocatechuic aldehyde, the constitution of which is known to be $[OH : OH : CHO = 1 : 2 : 4]$, is treated with ethylenic bromide, it is converted into *protocatechuic aldehyde ethylenic ether* or *homopiperonal*, which crystallises in long, silky needles melting at 50—51.5° and boiling at 299°. It forms a *phenylhydrazone* melting at 107—108° and an *oxime* melting at 75—75.5°. The latter, on dehydration, yields a *nitrile*, which crystallises in fine needles melting at 105°. On reduction with stannous chloride, the nitro-derivative obtained from catechol ethylenic ether yields, the corresponding *amido-derivative*, which is a heavy, thick liquid, insoluble in water, and boiling at 162° under a pressure of 9 mm. The *hydrochloride* of this base melts and decomposes at about 220°, the *picrate* at about 180°, and the *platino-chloride* at 213°. The diazo-derivative, on treatment with cuprous cyanide, yields a nitrile which is identical with the product obtained from homopiperonaloxime (see above). The *acid* resulting from its hydrolysis melts at 137°.

It should be noted that the dimethylic ether of catechol forms a nitro-derivative analogous to that yielded by catechol ethylenic ether, the nitro-group taking up the para-position with regard to one of the alkyloxy-groups. This behaviour may be contrasted with that of substances containing, like naphthalene, two aromatic nuclei, in which case the substituting nitro-group takes up the meta-position. N. L.

Oxidation of Pyrogallol in Presence of Alkalis. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 126, 1459—1467).—In presence of 3 molecules of potassium hydroxide, each molecule of pyrogallol combines with 3 atoms of oxygen, and the quantity of carbonic oxide formed amounts to 2·2 per cent. of the volume of oxygen absorbed (this vol., ii, 534). With sodium hydroxide, the results are practically identical.

In presence of 3 equivalents of barium hydroxide, on the other hand, each molecule of pyrogallol absorbs only about 1 atom of oxygen, whilst with 0·67 molecule or 1·33 equivalents, the quantity of oxygen absorbed is a little less than 2 atoms per molecule of pyrogallol present. These abnormal results are probably due to the fact that the product of oxidation separates as a precipitate.

With ammonia, the results are again different. If 3 molecules are present for each molecule of pyrogallol, the absorption of oxygen is at first very rapid, but eventually becomes much slower, and a considerable time is required to reach the limit of the reaction. Four atoms of oxygen are absorbed for each molecule of pyrogallol present, but the nitrogen of the ammonia is not oxidised to nitrate, although it may possibly be converted into an azo-compound. In presence of ammonia or barium hydroxide, the proportion of carbonic oxide formed is distinctly lower than in presence of sodium or potassium hydroxide.

The chief products of oxidation in presence of potassium or sodium hydroxide are a dark brown substance soluble in water and of the composition $(C_5H_5O_4)_m$ or $C_{20}H_{20}O_{16}$, and carbonic anhydride, which at once liberated on adding an excess of an acid to the alkaline solutions, although the liquid must be heated in order to expel the whole of the gas. A dark red, crystallisable compound, $C_{20}H_{20}O_{11}$, soluble in ether and having some of the properties of purpurogallin, is formed in the early stages of oxidation, whilst another compound, $(C_4H_4O_3)_n$, or probably $C_{16}H_{16}O_{12}$, also soluble in ether, is found amongst the final products in quantity equal to about 10 per cent. of the original pyrogallol. No definite evidence was obtained of the formation of any volatile acids. The quantity of the chief product, $C_{20}H_{20}O_{16}$, amounts to about 86 per cent. of the original pyrogallol.

The compound $C_{20}H_{20}O_{11}$ differs from purpurogallin, $C_{20}H_{16}O_9$, by $2H_2O$, and the product, $C_{20}H_{20}O_{16}$, differs from it by $2H_2O + O_5$. It would seem that the several products result from the condensation of 4 molecules of pyrogallol, but probably the condensation is not direct, and a compound of a quinone character, such as trihydroxyquinone, is first formed and subsequently split up thus, $4C_6H_4O_5 = C_{20}H_{16}O_{12} + 4CO_2$, the compound, $C_{20}H_{16}O_{12}$, afterwards combining with $2H_2O$ and O_2 . During the oxidation, the benzene ring breaks down, and probably is converted into a more complex cyclic compound of the same order, such as triphenylethane.

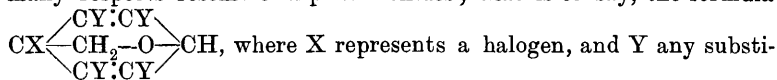
C. H. B.

Derivatives of Eugenol. By F. J. POND and F. T. BEERS (*J. Amer. Chem. Soc.*, 1897, 19, 825—831).—Two classes of unsaturated benzene derivatives which contain the group C_3H_5 joined to a benzene nucleus are known; those of the formula $R \cdot CH : CHMe$ yield dibromides which are converted by the action of sodium methoxide into ketones of the formula $R \cdot CO \cdot CH_2Me$, whereas those of the second class,

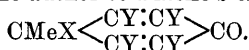
$R \cdot CH_2 \cdot CH : CH_2$, do not undergo this change. In order to extend the experimental evidence for this difference in properties, the authors have examined the behaviour of isoeugenol benzylic ether. *Eugenol benzylic ether*, $CH_2Ph \cdot O \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH : CH_2$, is prepared by the action of benzylic chloride on an alkaline solution of eugenol, and is a dark-coloured oil which boils and decomposes at about 235° . When it is heated with alcoholic potash, it is converted into *isoeugenol benzylic ether*, $CH_2Ph \cdot O \cdot C_6H_3(OMe) \cdot CH : CHMe$, which crystallises in long, white needles melting at 48° . The *dibromide* also crystallises in white needles, and melts at 122° . When this is treated with sodium methoxide, and the oily product boiled with dilute aqueous potash, it yields the *ketone*, $CH_2Ph \cdot O \cdot C_6H_3(OMe) \cdot CO \cdot CH_2Me$, which crystallises in small, white needles melting at 93° . The *oxime* crystallises in white needles melting at 118.5° , and readily yields the ketone when hydrolysed with dilute sulphuric acid.

Isoeugenol benzylic ether, therefore, behaves in a similar manner to the other propenyl derivatives of analogous constitution. A. H.

Derivatives of Aromatic β - and δ -Oxides. By KARL AUWERS (*Annalen*, 1898, 301, 203—266).—It is scarcely possible to do justice to this paper in an abstract. In a series of recent communications (compare Abstr., 1897, i, 335), the author has followed the action of bromine on phenols and phenol-alcohols, and, among the numerous compounds described in this connection, has drawn attention to certain products which, although insoluble in alkalis, are highly active in other respects. The methods of obtaining them are frequently too irregular to throw light on their constitution; the present paper, however, develops the formulæ theoretically possible, and discusses their probability, more particularly in relation to the views recently expressed by Zincke (this vol., i, 70). As a result of this discussion, the author is led to regard the bromo-compounds in question as derivatives of oxides, which in many respects resemble aliphatic oxides; that is to say, the formula

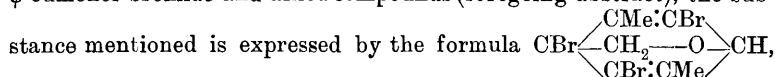


is preferred by the author to Zincke's expression,



The same considerations apply to the acetates of this type which do not dissolve in alkali. M. O. F.

New Derivatives of Dibromanhydroparahydroxy- ψ -cumylic Alcohol. By KARL AUWERS and NORMAN L. SHELDON (*Annalen*, 1898, 301, 266—282. Compare Abstr., 1897, i, 335).—According to the views developed by Auwers regarding the constitution of dibromo- ψ -cumenol bromide and allied compounds (foregoing abstract), the substance mentioned is expressed by the formula



and may be regarded as the bromide of dibromanhydroparahydroxy- ψ -cumylic alcohol; a preliminary account of the compounds described in this paper has already appeared (*loc. cit.*).

The *acetyl* derivative of dibromoparahydroxy- ψ -cumylic bromide, $\text{CH}_2\text{Br} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CMe} \end{smallmatrix} \text{C} \cdot \text{OAc}$, is obtained by heating the bromide of dibromanhydroparahydroxy- ψ -cumylic alcohol (m. p. 126°) with boiling acetic anhydride during 5 hours; it crystallises from glacial acetic acid in lustrous needles, and melts at 161° . The mother liquor contains the diacetyl derivative of dibromoparahydroxy- ψ -cumylic alcohol, which melts at $105\text{--}106^\circ$.

When the acetyl derivative is heated with absolute alcohol in sealed tubes at 100° , it is converted into the ethylic ether of dibromoparahydroxy- ψ -cumylic alcohol, $\text{OEt} \cdot \text{CH}_2 \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CMe} \end{smallmatrix} \text{C} \cdot \text{OH}$, which dissolves in alkali and melts at $86\text{--}87^\circ$ (compare Auwers and Marwedel, Abstr., 1896, i, 150); the *acetyl* derivative is produced along with it, and crystallises from alcohol in slender, white needles melting at $64\text{--}66^\circ$.

Dibromoparacetoxy- ψ -cumylaniline, $\text{NHPh} \cdot \text{CH}_2 \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CMe} \end{smallmatrix} \text{C} \cdot \text{OAc}$, prepared by heating a benzene solution of the tribromacetate (m. p. 161°) with aniline (2 mols.), crystallises from petroleum in lustrous octahedra melting at 120° ; hydrolysis with alcoholic alkali resolves it into *dibromoparahydroxy- ψ -cumylaniline* which melts at 134° (Auwers and Marwedel, *loc. cit.*).

The compound, $\text{C}_{22}\text{H}_{20}\text{Br}_4\text{O}_4$, prepared by heating an alcohol solution of the tribromacetate with sodium ethoxide (1 mol.) in a reflux apparatus, crystallises from hot petroleum in slender, lustrous needles, and melts at 175° . Alcoholic potash resolves the substance into the ethylic ether of dibromoparahydroxy- ψ -cumylic alcohol, which is also formed when the tribromacetate is warmed with alcoholic sodium ethoxide (2 mols.). Hydrogen bromide converts it into the compound, $\text{C}_{18}\text{H}_{16}\text{Br}_4\text{O}_2$, which crystallises from glacial acetic acid in lustrous needles, and melts at $217\text{--}220^\circ$.

When the diacetyl derivative of dibromoparahydroxy- ψ -cumylic alcohol is heated with alcoholic sodium ethoxide (1 mol.), it yields tetrabromodihydroxytetramethylstilbene (Abstr., 1896, i, 150). Under the influence of sunlight, bromine in glacial acetic acid converts the diacetyl compound into dibromopara-xyloquinone (m. p. $181\text{--}182^\circ$), diffused light causing it to yield the acetyl derivative melting at 161° ; if carbon bisulphide is used in place of glacial acetic acid, the bromide of dibromanhydroparahydroxy- ψ -cumylic alcohol (m. p. 126°) is formed. The latter compound is also produced when hydrogen bromide is passed into a solution of the diacetyl derivative in glacial acetic acid at 70° , the tribromacetate (m. p. 161°) being formed at ordinary temperatures.

The *acetyl* derivative of dibromoparahydroxy- ψ -cumylic alcohol, $\text{OH} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CMe} \end{smallmatrix} \text{C} \cdot \text{OAc}$, prepared from the diacetyl derivative by heating the solution in acetone and water with caustic soda (1 mol.), crystallises from petroleum in small, lustrous needles, and melts at $120\text{--}121.5^\circ$.

An isomeric tribromo- ψ -cumenol has been obtained as a bye-product

in the preparation of dibromo- ψ -cumenol bromide (Abstr., 1896, i, 423); although the melting point as originally given is 181° , later preparations melted at 175° . The *acetyl* derivative crystallises from methylic alcohol in flat, lustrous needles, and melts at 122 — 124° ; hydrolysis regenerates tribromo- ψ -cumenol melting at 180° . M. O. F.

Mercury Compounds of Organic Bases. By LEONE PESCI (*Zeit. anorg. Chem.*, 1897, 15, 208—233).—The paper contains a concise account of the various mercury compounds of organic bases, which have at various times been prepared by the author and his pupils, and is divided into the following chapters: I. *Mercurioanilido-compounds* (compare Abstr., 1892, 1448; 1894, i, 248; 1897, i, 559; 1893, ii, 278; 1893, i, 322). II. *Mercury compounds of methylaniline* (Abstr., 1893, i, 24; 1894, i, 248). III. *Mercury compounds of dimethylaniline* (Abstr., 1894, i, 248). IV. *Mercury compounds of ethylaniline* (Abstr., 1894, i, 249). V. *Mercury compounds of diethylaniline* (Abstr., 1894, i, 249). VI. *Mercury compounds of benzyllaniline* (Abstr., 1897, i, 337). VII. *Mercury compounds of acetanilide* (Abstr., 1895, i, 357, 358). VIII. *Mercury compounds of benzylamine* (Abstr., 1897, i, 36). IX. *Mercurioquinoline compounds* (Abstr., 1896, i, 186). X. *Mercuropyridine compounds* (Abstr., 1896, i, 388). XI. *Mercury α -picoline compounds* (Abstr., 1897, i, 370). XII. *Mercuriopiperidine compounds* (Abstr., 1897, i, 370). XIII. *Mercuriocarbamide and its salts* (Abstr., 1897, i, 328). A. W. C.

Mercury Compounds of Dimethylparatoluidine and of Paratoluidine. By LEONE PESCI (*Zeit. anorg. Chem.*, 1898, 17, 276—283).—Compounds obtained by the action of mercury salts on non-substituted anilines contain the mercury atom in the para-position, whereas the compounds of dimethylparatoluidine and of paratoluidine contain the mercury which is combined with the aromatic nucleus in the meta-position relatively to the methyl group. This is proved by the synthesis of mercury dimethylparatoluidine by heating metabromodimethylparatoluidine with ethylic acetate and sodium amalgam at 120 — 125° for 48 hours.

Mercuryditoluylenetetramethylmercuridiammonium compounds contain the bivalent radicle $\text{Hg} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2 \\ \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2 \end{smallmatrix} \right\rangle \text{Hg}$ [$\text{Me} : \text{Hg} : \text{NMe}_2 = 1 : 3 : 4$].

The *hydroxide*, $\text{Hg}(\text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2 \cdot \text{OH})_2\text{Hg}$, obtained by allowing the acetate to remain for 24 hours with concentrated potassium hydroxide, crystallises in colourless, microscopic needles, sinters at 114° , melts at 117° , is only sparingly soluble in cold water, but very easily in methylic alcohol or benzene. The *acetate*, obtained by adding an alcoholic solution of dimethylparatoluidine to a solution of mercury acetate in dilute alcohol, crystallises in colourless, lustrous needles, melts at 131.5° , is easily soluble in methylic alcohol, less so in ethylic alcohol, and insoluble in water. The *nitrate*, obtained by treating an alcoholic solution of the acetate with calcium nitrate, crystallises in colourless needles and melts at 131° . The *chloride* crystallises in slender needles and melts at 159 — 159.5° ; the *bromide* in lustrous

needles melting at 149—150°, and the *iodide* in yellow needles melting at 126°.

Mercurydimethylparatoluidine, $\text{Hg}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}_2)_2$, obtained by the action of sodium thiosulphate on the above hydroxide suspended in water, crystallises from boiling alcohol in colourless, lustrous leaflets, melts at 60°, is easily soluble in benzene, and when treated with mercury iodide, bromide, chloride, and acetate, yields the salts described above. The mercurydimethylparatoluidine obtained by synthesis from metabromodimethylparatoluidine is in every respect identical with this product.

Mercuryditoluylenemercuridiammonium compounds containing the radicle $\text{Hg}(\text{C}_6\text{H}_3\text{MeNH}_2)_2\text{Hg}$ [$\text{Me} : \text{Hg} : \text{NH}_2 = 1 : 3 : 4$].

The *hydroxide*, obtained by the action of potassium hydroxide on the acetate, crystallises in yellowish leaflets, begins to decompose at 120°, melts at 212—213°, has a strongly alkaline reaction, and is insoluble in most solvents. The *acetate*, obtained by the action of mercury acetate on paratoluidine, crystallises in leaflets, melts at 184°, and is easily soluble in benzene, alcohol, or ether, but insoluble in water. The *chloride* crystallises in prisms and melts at 170°.

Mercuryparatoluidine, $\text{Hg}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2)_2$, obtained by heating the preceding hydroxide with sodium thiosulphate, crystallises from boiling alcohol in four-sided leaflets, melts at 156°, and is insoluble in most of the ordinary solvents. It cannot be prepared from the metabromoparatoluidine, but most probably has the same constitution as the preceding mercury dimethylparatoluidine. E. C. R.

Electro-synthesis of Anhydroparamidobenzyl Alcohol. By WALTHER LÖB (*Ber.*, 1898, 31, 2037—2038).—The electrolytic reduction of a mixture of nitrobenzene and formaldehyde in acid solution yields two different products according to the current density at the cathode. With a high current density, anhydroparahydroxylaminobenzyl alcohol is obtained, and with a low density and at low temperatures the substance formed is produced from 3 molecules of formaldehyde and 2 of nitrobenzene by reduction.

Under special conditions, anhydroparamidobenzyl alcohol may be obtained. One part of formaldehyde (in 40 per cent. solution) and 25 parts of concentrated hydrochloric acid are added to a solution of 1 part of nitrobenzene in 40 parts of alcohol, and the mixture reduced by the use of a platinum cathode, the current density of which is $\text{ND}_{100} = 0.5$ ampère, whilst the temperature is kept at about 12°. The clear, reddish-yellow solution, when freed from alcohol and rendered alkaline, yields anhydroparamidobenzyl alcohol. J. J. S.

Some Amidoketones. By HUGH RYAN (*Ber.*, 1898, 31, 2129—2133).—*Ethyllic metaxylylacetoacetate*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{COMe})\cdot\text{COOEt}$, obtained by the action of metaxylylic bromide on the sodium compound of ethyllic acetoacetate, is a yellowish oil which distils at 195° under a pressure of 36 mm.; it dissolves slowly in dilute alkali, and yields a crystalline sodium salt when shaken with strong soda. By acting on this compound with nitrous acid under varied conditions, *isonitroso-metaxylylacetic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{C}(\text{:NOH})\cdot\text{COOH}$, and *isonitroso-*

metaxylylacetone, $C_6H_4Me \cdot CH_2 \cdot C(:N \cdot OH) \cdot COMe$, are obtained. The former crystallises in colourless needles and melts at 139° ; its *silver* salt has the composition $C_{10}H_{10}AgNO_3$. The latter dissolves readily in ether, alcohol, and benzene, forms aggregates of needles, and melts at $54-55^\circ$; its solution in alkalis is yellow. *Amidometaxylylacetone*, $C_6H_4Me \cdot CH_2 \cdot CH(NH_2) \cdot COMe$, is prepared from the isonitrosoketone by reduction with tin and hydrochloric acid; the hydrochloride, $C_{11}H_{15}NO \cdot HCl$, is crystalline, melts at $150-151^\circ$, and reduces warm Fehling's solution; the *stannichloride*, $(C_{11}H_{15}NO)_2 \cdot H_2SnCl_6$, is colourless, and melts at $177-178^\circ$; the *platinochloride*, $(C_{11}H_{15}NO)_2 \cdot H_2PtCl_6$, forms yellow crystals and melts at 187° ; the *picrate*, $C_{11}H_{15}NO \cdot C_6H_3N_3O_7$, melts at 87° . The hydrochloride of the foregoing base, when treated with potassium thiocyanate, yields *metaxylylmethylimidazolylmercaptan*, $C_8H_9 \cdot \begin{array}{c} \text{C} \text{---} \text{N} \\ | \quad \diagup \\ CMe \cdot NH \end{array} > C \cdot SH$ or $C_8H_9 \cdot \begin{array}{c} CMeN \\ | \quad \diagup \\ C \text{---} NH \end{array} > C \cdot SH$, which forms microscopic crystals melting at 267° ; if potassium cyanate is employed, *metaxylylmethylimidazolone*, $C_8H_9 \cdot \begin{array}{c} \text{C} \text{---} NH \\ | \quad \diagup \\ CMe \cdot NH \end{array} > CO$, melting at 265° , is produced.

Paramethyl- α -phthalimidoacetophenone, $C_6H_4Me \cdot CO \cdot CH_2 \cdot N : C_8H_4O_2$, is prepared by heating paramethyl- α -chloracetophenone with potassium phthalimide; it forms octahedra-like crystals, dissolves readily in hot glacial acetic acid, and sparingly in alcohol and ether; it is insoluble in water, and melts at $175-176^\circ$; its phenylhydrazone,

$C_6H_4Me \cdot C(:N_2 \cdot HPh) \cdot CH_2 \cdot N : C_8H_4O_2$, forms beautiful, yellow needles, and melts at 154° . The corresponding *phthalamic acid*, $C_6H_4Me \cdot CO \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$, melts at 165° and gives a blue, crystalline *copper* salt and a white, crystalline *silver* salt, $C_{17}H_{14}AgNO_4$; when boiled with hydrochloric acid, it is hydrolysed, yielding phthalic acid and *paramethyl- α -amidoacetophenone hydrochloride*, $C_6H_4Me \cdot CO \cdot CH_2 \cdot NH_2 \cdot HCl$. This crystallises from alcohol in colourless needles, and melts at 206° , forming a red liquid; its solution instantly reduces Fehling's solution, and, on treatment with alkali, yields the free base, which at once reddens and decomposes. The *aurochloride* of the base, $C_9H_{11}NO \cdot HAuCl_4$, crystallises in long needles melting at 167° ; the *platinochloride*, $(C_9H_{11}NO)_2 \cdot H_2PtCl_6$, crystallises from hot water in long prisms melting at 206° ; the *picrate*, $C_9H_{11}NO \cdot C_6H_3N_3O_7$, crystallises from alcohol in yellow needles melting at 176° . A. L.

Action of Amines on Acylimido-ethers: Acylamidines. By HENRY L. WHEELER and PERCY T. WALDEN (*Amer. Chem. J.*, 1898, 20, 568-576).—In the production of the acylamidines from acylimido-ethers (compare this vol., i, 185), it is probable that an additive product is first formed, which is subsequently decomposed; thus from benzoylbenzimidomethylic ether and ammonia, the derivative $OMe \cdot CPh(NH_2) \cdot NHBz$ would be first produced, and its decomposition would give rise to a substance having one of the two formulæ,

I. $NH : CPh \cdot NHBz$, or II. $NH_2 \cdot CPh : NBz$.

The benzoylbenzamidine actually obtained by the author in this

reaction is identical with the substance to which Pinner attributed the first of these formulæ, since it was readily converted into dibenzamide by the loss of ammonia. This decomposition, however, cannot be looked on as satisfactorily establishing the constitution of Pinner's benzoylbenzimidine; for assuming that the hydrolysis takes place through an initial addition of H_2O , the same additive product, $\text{NH}_2\cdot\text{CPh}(\text{OH})\cdot\text{NHBz}$, would be formed from both the amidines I and II, and both the latter could therefore give rise to dibenzamide and ammonia. That such decompositions afford no clue to the structure of amidines is shown by the behaviour of the similarly constituted benzoylbenzimidido- and benzoylphenylacetamido-ethyl ethers on hydrolysis; whereas the former, $\text{OEt}\cdot\text{CPh}\cdot\text{NBz}$, gives rise to dibenzamide and alcohol, the latter, $\text{OEt}\cdot\text{C}(\text{C}_7\text{H}_7)\cdot\text{NBz}$, yields benzamide and phenylethyl acetate (*loc. cit.*).

Beckmann and Sandel (Abstr., 1897, i, 564) have stated that benzoylbenzimidide chloride, $\text{NBz}\cdot\text{CPhCl}$, unites readily with ammonia and primary amines to form amidines, but that it does not combine with secondary amines; the authors find similarly that the acylimidoethers are not acted on by secondary bases.

Benzoylbenzimidine, prepared by warming an alcoholic solution of benzoylbenzimidopropyl ether with aqueous ammonia, is identical with the substance obtained by Pinner on dissolving benzonitrile in fuming sulphuric acid; both melt at $100\text{--}101^\circ$, not at 106° as stated by Pinner. The *hydrochloride*, $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}\cdot\text{HCl}$, melts at about 190° , and is decomposed by water; the *platinochloride*, $(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2\cdot\text{H}_2\text{PtCl}_6$, on being heated, darkens at $225\text{--}230^\circ$, and melts at 240° .

Benzoylethylbenzimidine, prepared from ethylamine and benzoylbenzimidopropyl ether, melts at 88° , and is probably identical with the substance obtained by Lossen (Abstr., 1892, 51) from ethylbenzimidine and benzoic chloride.

Benzoylphenylbenzimidine, prepared from benzoylbenzimidioethyl ether and aniline, melts at 143° , and has been described by Beckmann and Sandel (*loc. cit.*); methylaniline and ethylaniline do not interact with benzoylbenzimidioethyl ether.

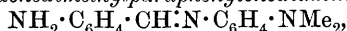
Acetylphenylbenzamidine, $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$, prepared from acetylbenzimidioethyl ether and aniline, separates from alcohol in colourless crystals, and melts at $138\cdot5^\circ$; *acetylparatolylbenzamidine* melts at $136\cdot5^\circ$, whilst *acetylmetachlorophenylbenzamidine* melts at $128\text{--}129^\circ$. *1:3:4-Xylolbenzamidine* is formed when 1:3:4-xylidine is left in contact with acetylbenzimidioethyl ether, the acetyl group being removed; it crystallises from light petroleum in long, colourless needles, and melts at 106° . *Acetyl-β-naphthylbenzamidine*, from β-naphthylamine and acetylbenzimidioethyl ether, melts at 137° ; and *propionylphenylbenzamidine* from aniline and the corresponding imido-ether, at 138° . Attempts to prepare normal butyrylbenzamidine by dissolving butyrylbenzimidioethyl ether in dilute alcoholic ammonia failed, benzamide being formed; the same result was obtained by similarly treating acetyl- and propionylbenzimidioethers,

Normal butyrylphenylbenzamidine, prepared from butyrylbenzimidioethyl ether and aniline, separates from alcohol in colourless prisms, and melts at 137° .

W A. D.

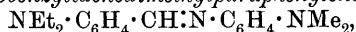
Aromatic Azomethine Compounds. By RICHARD MÖHLAU (*Ber.*, 1898, 31, 2250—2261. Compare *Abstr.*, 1893, i, 470).—The compounds produced by the action of aromatic aldehydes on primary aromatic bases possess a constitution somewhat analogous to that of azo-derivatives, and also resemble these in the possession of tinctorial properties. These properties are due to the chromophoric group $-N:CH-$, which corresponds with the azo-group in azo-colours. Azomethine compounds, analogous to basic and acidic azo-derivatives, have already been prepared (*Abstr.*, 1895, i, 214 and 221), whilst the following are described for the first time.

Paramidobenzylidenedimethylparaphenylenediamine,



is termed by the author *anhydroparamidobenzaldehydeparamidodimethylaniline*, similar names being given to the other compounds described. It is obtained by heating together a hydrochloric acid solution of paramidobenzaldehyde and paramidodimethylaniline; the free base crystallises from dilute methylic alcohol in yellow leaflets melting at $191-192^\circ$, and it is hydrolysed by acids, yielding its components.

Paradiethylamidobenzylidenedimethylparaphenylenediamine,



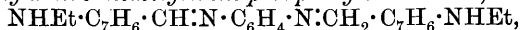
produced on heating together paraformaldehyde, diethylaniline, and nitrosodimethylaniline in presence of hydrochloric acid, crystallises from methylic or ethylic alcohol in yellow prisms melting at $140-141^\circ$. The *hydrochloride* forms red, prismatic crystals with a steel-blue reflex.

Bis-paradimethylamidobenzylidene-paraphenylenediamine,



melts at 190° . The corresponding *ethyl* compound, obtained by adding nitroso-dimethylaniline hydrochloride to a solution of paraformaldehyde and diethylaniline in hydrochloric acid, and subsequently treating the product with alkalis, crystallises from dimethylaniline in golden-yellow needles, and melts at $206.5-207.5^\circ$. The *hydrochloride* forms red needles with a steel blue reflex, and contains $7H_2O$.

Bis-parethylamidometatolylidene-paraphenylenediamine,



is obtained by the above reaction from ethylorthotoluidine, which appears to behave like a tertiary aromatic amine; the condensation product crystallises from dimethylaniline in dark yellow, lustrous prisms, and melts at $234-235^\circ$. Several phenolic azomethine derivatives corresponding with hydroxy-azo-compounds are already known (*Abstr.*, 1888, 50, and 1893, i, 273), and the following are obtained by condensing paranitrobenzaldehyde with the three amidonaphthols in alcoholic solution in the presence of acetic acid.

1:4-*Paranitrobenzylideneamidonaphthol* crystallises from alcohol in scarlet leaflets, and melts at 171° ; it dissolves in aqueous alkalis, forming a cherry-red solution, and with alcoholic soda it develops a deep violet coloration. The 1:2-compound forms scarlet prisms with a golden lustre, and melts at 174° ; aqueous solutions of its salts are red, whilst their alcoholic solutions are violet. The 2:1 compound, which

crystallises from alcohol in orange needles and melts at 187° , is insoluble in aqueous alkalis, but develops a violet coloration with alcoholic soda.

These three isomerides are all hydrolysed into their components when their solutions in concentrated sulphuric acid are diluted with water. Schiff (Abstr., 1882, 303) has previously obtained azomethine compounds corresponding with azocarboxylic acids. The azomethine analogues of "Alizarine yellow R" and "Alizarine yellow 2G" are now described.

Paranitrobenzylidene-5-amidosalicylic acid results from the condensation of 1:2:5-amidosalicylic acid with paranitrobenzaldehyde in alcoholic solution; it crystallises from dilute alcohol in golden-yellow needles, and decomposes at $217-218^{\circ}$. It closely resembles its azo-analogue. The *metanitro*-compound, prepared by substituting metanitrobenzaldehyde for its para-isomeride, crystallises in pale yellow needles, and decomposes at 252° . The *orthonitro*-compound, obtained from orthonitrobenzaldehyde, forms lemon-yellow needles, and decomposes at 221° . In the case of these three azomethine derivatives, it is found that their basic alkali salts have the same colour as the normal salts of the corresponding azo-colours. G. T. M.

Formation of Salts and Hydrates of Azophenol. By JOHN T. HEWITT, T. S. MOORE, and A. E. PITT (*Ber.*, 1898, 31, 2114—2123. Compare Abstr., 1894, i, 123; 1895, i, 353, &c.).—*Orthobromobenzeneazophenol*, $C_6H_4Br \cdot N_2 \cdot C_6H_4 \cdot OH$, may be obtained in a hydrated form, as well as in an anhydrous state. The former, $C_{12}H_9BrN_2O \cdot \frac{1}{2}H_2O$, is yellow, melts at 85° , and yields the anhydrous form when gently warmed. The latter is red, and melts at 97° ; it is readily soluble in acetone and in nitrobenzene, but dissolves only sparingly in light petroleum. The *hydrochloride* is dark red, and melts between 116° and 127° , hydrogen chloride being evolved; the *acetate*, which forms bright yellow crystals melting at 89° , dissolves in the ordinary solvents with the exception of light petroleum. The *benzoate* forms orange crystals, and melts at $122-123^{\circ}$; the *benzenesulphonate* melts at 69° .

Parabromobenzeneazophenol, $C_6H_4Br \cdot N_2 \cdot C_6H_4 \cdot OH$, crystallises from toluene in brownish-red needles melting at 157° . The *hydrochloride* is bright red, melts at $171-177^{\circ}$, and does not afford a hydrated azophenol on treatment with water. The *acetate* crystallises from ethylic acetate in orange needles melting at 158° . The *benzoate* crystallises in beautiful, bright yellow leaflets, and melts at 166° , whilst the *benzenesulphonate* forms bright yellow crystals, and melts at 136° .

Metatolueneazophenol hydrochloride, when decomposed with water, yields a *hydrate*, $(C_{13}H_{22}N_2O)_2 \cdot H_2O$, which may also be obtained by dissolving the anhydrous form in sulphuric acid, and then adding water; it forms small, bright yellow leaflets, and darkens in colour when heated at 90° .

Orthophenetolazophenol hydrochloride, $C_{14}H_{14}N_2O_2 \cdot HCl$, is dark red, and melts at $125-131^{\circ}$; it yields only the anhydrous modification of the azophenol, and therefore differs in this respect from the other ortho-substituted azophenols which have been examined.

The *benzoate* separates from alcohol in red needles, and melts at 99° ; the *benzenesulphonate* crystallises from boiling alcohol in large, red needles, and melts at 84° .

Metaphenetoilazophenol hydrochloride is deep rose-red, and melts at 140 — 150° ; it yields a hydrated azophenol, $(C_{14}H_{14}N_2O_2)_2 + H_2O$, which melts at 89 — 91° . The *benzenesulphonate* separates from dilute alcohol in aggregates of bright-red needles, and melts at 77° .

Paraphenetoilazophenol hydrochloride is of a carmine colour, and decomposes at 132 — 160° ; when treated with water, it yields a hydrated modification, $C_{14}H_{14}N_2O_2 + H_2O$, of the parent substance, which melts at 105 — 110° ; this melting point is in close agreement with that observed by Riedel (D.R.-P. 48543), and accounts for the difference between the melting points given by him and by Jacobson (Abstr., 1896, i, 27), who was dealing with the anhydrous form. The *acetate* of paraphenetoilazophenol forms yellow leaflets and melts at 119° . The *benzoate* forms brownish-red crystals, and melts at 127° , whilst the *benzenesulphonate* separates from boiling alcohol in large, brown leaflets which melt at 105° .

Orthonitrobenzeneazophenol does not form a stable hydrochloride, a fact probably due to the weakening of the basicity produced by a strongly negative group in the ortho-position, and not to any steric hindrance to chemical action. *Metanitrobenzeneazophenol hydrochloride*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH, HCl$, melts at 167 — 171° ; *paranitrobenzeneazophenol hydrochloride* is dark-red, and melts and slowly decomposes at 158 — 167.5° . Neither of these two compounds yields a hydrated azophenol on treatment with water.

The authors finally draw some general conclusions, for which the original paper must be consulted.

A. L.

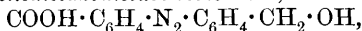
Electro-synthesis of Mixed Azo-compounds. By WALTHER LÖB (*Ber.*, 1898, 31, 2201—2205).—Kauffmann and Hof have shown that when metanitrobenzaldehyde is electrolytically reduced in alkaline solution, the chief product is metazobenzoic acid together with a small quantity of metazobenzyl alcohol. They sought to explain this preponderance of acid by supposing that the nitrobenzyl alcohol, under the action of the alkali, is converted into azoxybenzyl alcohol and azoxybenzoic acid according to the equation $8NO_2 \cdot C_6H_4 \cdot CH_2 \cdot OH \rightleftharpoons 3(COOH \cdot C_6H_4)_2N_2O + (OH \cdot CH_2 \cdot C_6H_4)_2N_2O + 6H_2O$, and that these, on electrolysis, yield the corresponding azo-compounds. This supposition is considered by the author to be untenable, since no trace of the sparingly soluble azoxy-compounds could be detected during the electrolysis. It is also shown that the azo-acid consists of only a small amount of metazobenzoic acid, the chief product being a mixed azo-derivative, $COOH \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot CH_2 \cdot OH$.

Direct experiment has shown that when equivalent quantities of two nitro-derivatives in alkaline solution are reduced at the cathode, a mixed azo-compound is always formed. Under suitable conditions, the positions of the substituting groups are without influence, so that practically any azo-compounds may be obtained by this method, whereas Griess's method yields only amido- or hydroxy-derivatives with the substituting groups in the para- or ortho-position.

It has not been found possible to electrolytically reduce nitrophenols to azophenols.

If lead electrodes are employed, the reduction often proceeds as far as the formation of hydrazo-derivatives; the best yield of azo-compound is obtained with platinum or mercury electrodes.

Exo-hydroxytoluenemetazometabenzoic acid,



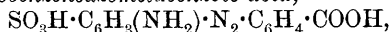
obtained by the reduction of metanitrobenzaldehyde, crystallises from alcohol in yellow plates melting at $182-183^\circ$, and is readily soluble in alcohol or ether, but insoluble in water.

Toluenepara-azometabenzoic acid, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, from paranitrotoluene and metanitrobenzoic acid, melts at 192° and is readily soluble in ether or alcohol.

Metasulphobenzeneazometabenzoic acid, $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, from nitrobenzenesulphonic acid and metanitrobenzoic acid, crystallises in yellow plates which decompose when heated. It is insoluble in ether, but dissolves readily in water or alcohol.

Paramidobenzeneazometabenzoic acid, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, from paranitraniline and metanitrobenzoic acid, crystallises in yellowish-red needles, is readily soluble in alcohol, sparingly in hot water, and insoluble in ether.

Paramidosulphobenzeneazometabenzoic acid,



forms yellowish-red crystals, dissolves in water, and gives, on addition of acids, a blood-red coloration, and of alkalis, an intense yellow coloration.

Paradimethylamidobenzeneazometabenzoic acid, obtained from metanitrobenzoic acid and paranitrodimethylaniline, has already been described by Griess.

J. J. S.

Additive Compounds of Diazonium-haloids with Phenols and with Acetic Acid. By ARTHUR R. HANTZSCH (*Ber.*, 1898, 31, 2053—2057).—Diazonium haloids readily dissolve in both phenol and acetic acid, and in several cases well-defined, crystalline additive compounds can be obtained on the addition of benzene. All these additive compounds are extremely unstable and are immediately decomposed into their constituents by water, alcohol, or ether. The yellow phenol derivatives are more stable than the corresponding acetic acid compounds; similar additive compounds are formed with formic acid, but they cannot be obtained in a crystalline condition. Homologues of phenol, the cresols, for example, also yield crystalline products; resorcinol and β -naphthol, on the other hand, at once combine to yield azo-dyes. No additive compounds can be obtained with ethylic acetoacetate or with ethylic malonate, although many diazonium chlorides are soluble in these ethereal salts. Diazonium haloids appear to form additive compounds most readily, diazonium nitrates not so readily, and the sulphates not at all.

Diazonium chloride or bromide dissolves in crystallised phenol (2 mols.) forming a red oil, but no crystalline derivatives are formed.

Parabromodiazonium chloride phenate, $\text{C}_6\text{H}_4\text{Br} \cdot \text{N}_2\text{Cl} \cdot 2\text{PhOH}$, is most

easily obtained by dissolving the diazo-salt (1 gram) in a mixture of phenol (2.5 grams) and benzene (5 grams); on the addition of light petroleum, a reddish oil separates which rapidly sets to a mass of yellow needles. It melts at 83—85°, but decomposes at the same time; although not soluble in benzene, it dissolves in a mixture of benzene and phenol. *Parabromodiazonium nitrate phenate*, obtained in a similar manner, also crystallises in yellow needles, melting and decomposing at 55—60°. *Paratoluenediazonium chloride* and *pseudocumenediazonium chloride phenates* could not be obtained in a solid form. *Tribromodiazonium bromide phenate* crystallises in yellow needles, and is even less stable than the monobromo-compound.

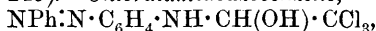
Parabromodiazonium chloride acetate, $C_6H_4Br \cdot N_2Cl \cdot C_2H_4O_2$, is obtained when benzene is added to a solution of parabromodiazonium chloride (1 gram) in glacial acetic acid (1 gram); it is first deposited as an oil, but quickly solidifies to a mass of colourless needles; it is extremely unstable and readily loses acetic acid.

Parabromodiazonium bromide acetate, $C_6H_4Br \cdot N_2Br \cdot C_2H_4O_2$, also crystallises in colourless needles and decomposes between 85° and 90°; after remaining for some six days in a desiccator, it is completely resolved into its constituents. Tribromodiazonium bromide does not combine with acetic acid, and bromodiazonium nitrate yields only an oily additive compound.

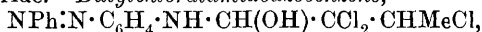
In this connection, the author mentions the results obtained by Ley on examining the cryoscopic behaviour of diazonium salts in acetic acid, and compares these with similar results obtained with lithium chloride.

J. J. S.

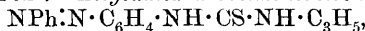
Derivatives of Amidoazobenzene. By MARIO BETTI (*Gazzetta*, 1898, 28, i, 241—245).—*Chloralamidoazobenzene*,



obtained by heating a mixture of chloral and amidoazobenzene with a little alcohol on the water bath, crystallises in yellow scales melting at 127°, and is converted into acetamidoazobenzene on boiling with acetic anhydride. *Butylchloralamidoazobenzene*,



prepared in an analogous manner, crystallises in yellow scales melting at 96—97°. *Furfurylideneamidoazobenzene*, $NPh \cdot N \cdot C_6H_4 \cdot N : CH \cdot C_4OH_3$, obtained by heating furfuraldehyde with amidoazobenzene, crystallises in red needles melting at 129—130°. *Salicylideneamidoazobenzene*, $NPh \cdot N \cdot C_6H_4 \cdot N : CH \cdot C_6H_4 \cdot OH$, prepared by heating salicylaldehyde with amidoazobenzene, crystallises in red scales melting at 155°. *Formylamidoazobenzene*, $NPh \cdot N \cdot C_6H_4 \cdot NH \cdot CHO$, is prepared from ethylic formate and amidoazobenzene, and is a yellow, crystalline substance melting at 162°. *Allylamidoazobenzenethiocarbamide*,



obtained by heating amidoazobenzene with mustard oil, crystallises in yellow needles melting at 133—134°.

W. J. P.

Preparation of Phenylamidoazobenzene and Azophenine. By T. LYNTON BRIGGS (*J. Soc. Chem. Ind.*, 1895, 14, 851—852).—The following method of preparing phenylamidoazobenzene on the large scale gives better results and is more rapid than the process described

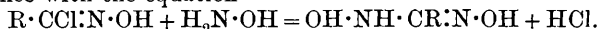
by Witt (*Ber.*, 1879, 12, 259); it is analogous to the latter's method of preparing tropæoline OO (potassium phenylamidoazobenzenesulphonate). Diphenylamine (34 parts) is dissolved in phenol, and after cooling as much as possible without allowing crystallisation to take place, agitated during several hours with an ice cold solution of diazobenzene chloride; the latter is prepared by the interaction of 20 parts of aniline, 14.5 parts of sodium nitrite, and 44 parts of dilute hydrochloric acid (sp. gr. = 1.162). The crude phenylamidoazobenzene is freed from phenol by agitation with warm concentrated caustic soda.

Azophenine can be conveniently prepared by heating phenylamidoazobenzene (50 parts) with aniline (100 parts) and aniline hydrochloride (5 parts) during 24 hours at 50°. If a larger quantity (60 parts) of aniline hydrochloride be employed, and the mixture heated during the first few hours at 100—130°, subsequently at 160—180° during 24 hours, the dye-stuff "induline G O" is obtained. W. A. D.

Action of Nitric Peroxide on Nitrosophenols. By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1898, 28, i, 305—310).—Nitric peroxide acts on quinoneoximes or nitrosophenols with formation of dinitrophenols in which the two nitro-groups are in the ortho- and para-positions relatively to the hydroxyl group. Ethereal solutions of the nitroso-compounds and nitric peroxide were used in the work.

Nitrosophenol, under these conditions, yields 2:4-dinitrophenol, and nitro-orthocresol, the 3:5-dinitro-orthocresol melting at 85—86°; nitrosothymol similarly gives the 3:5-dinitro-1-propyl-2-phenol melting at 55°, whilst β -naphthaquinoneoxime yields Martius's 2:4-dinitro-1-naphthol melting at 138°. W. J. P.

Hydroxylamidoximes. A New Series of Hydroxylamine Derivatives. By HEINRICH LEY (*Ber.*, 1898, 31, 2126—2129).—Hydroxylamine reacts with the chlorides of hydroxamic acids in accordance with the equation



Hydroxylamine hydrochloride is dissolved in the smallest possible amount of alcohol, and mixed with the calculated quantity of sodium ethoxide, excess of the latter being carefully avoided; the solution is then freed from sodium chloride by filtration, mixed with an ethereal solution of the chloride of benzhydroxamic acid, allowed to remain for 12 hours, and evaporated in a vacuum. The residue is now shaken with ether, which dissolves the new oxime, and, on evaporation, leaves it as an oil which crystallises when triturated with a few drops of benzene.

The product obtained by chlorinating benzaldoxime in chloroform solution, after being freed from hydrogen chloride by exposure in a vacuum desiccator containing potash and paraffin, may be used instead of the purified chloride in the above reaction.

Benzenylhydroxylamidoxime, $OH \cdot NH \cdot CPh : N \cdot OH$, crystallises from light petroleum and ethylic acetate in beautiful, shining, tabular crystals, and dissolves readily in alcohol, ether, benzene, and water, but is insoluble in light petroleum; it decomposes at 115°, evolving a large quantity of gas. Like Bamberger's azohydroxamides and the author's oxyamidine (this vol., i, 252), its solution in alcohol or water gives a

blue coloration with ferric chloride, and possesses weak acidic properties, giving a *copper* salt, $C_{14}H_{14}N_4O_4Ca$, which crystallises in microscopic leaflets. Its aqueous solution gives a pure yellow precipitate with mercuric chloride, and a blue coloration with ammonia and alkalis. The presence of the $NHOH$ group in the molecule is shown by the fact that it instantly reduces ammoniacal silver nitrate and Fehling's solution in the cold.

When the substance is mixed with cold acetic anhydride, a vigorous evolution of gas occurs and benzonitrile is formed; this behaviour would lead one to suppose that it possesses the structure

$$\begin{array}{c} \text{Ph} \cdot \text{C} \cdot \text{NH} \cdot \text{OH} \\ || \\ \text{N} \cdot \text{OH} \end{array}$$

analogous to that of the syn-oximes. A. L.

Tinctorial Reactions. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 449—455).—Weighed quantities of wool were treated with water, very dilute hydrochloric acid, and solutions of various basic colouring matters, the residual liquids being afterwards examined and the electrical conductivity determined in each case. The liquid obtained by boiling wool with water, or by digestion therewith at 75° , is neutral to litmus and phenolphthalein; it contains ammonia and, apparently, other nitrogenous basic substances, besides salts of lime and traces of oxide of iron, alumina, magnesia, potash, and soda. The amount of dissolved matter and the conductivity of the liquid depend on the time and temperature of the extraction, and on the previous washings of the wool. When wool is digested at 75° with $\frac{1}{2000}$ normal hydrochloric acid, the liquid acquires a conductivity equal to that of solutions of the chlorides of ammonium or calcium of equivalent strength, and it is found, in fact, that the whole of the acid remains in solution and is neutralised by the basic substances extracted from the wool. If, on the other hand, the wool is first extracted with water, and hydrochloric acid is then added to the filtered liquid, the conductivity of the liquid is but little less than that due to the acid alone. When digested with $\frac{1}{2000}$ normal solutions of magenta, chrysoidin, and vesuvin, the colour-base is fixed by the wool, whilst the acid remains in solution in combination with the basic substances extracted from the fibre. The conductivity of the exhausted dye-bath is accordingly found to be equal to that of the liquid obtained by the action on wool of $\frac{1}{2000}$ normal acid alone. The results of these experiments are in accordance with Knecht's theory that in dyeing with basic dyes there is a true double decomposition between the colouring matter and the substance of the fibre. N. L.

Action of Nitric Acid on Benzamide, Phenylacetamide, and Phenylpropionamide. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1897, 16, 253—256. Compare *Abstr.*, 1897, i, 619, and this vol., i, 588).—The nitration was effected at low temperatures, and in each case 1 gram of the amide was added, little by little, to 5 grams of pure nitric acid cooled by ice cold water, and the mixture then poured into 10 times its weight of iced water. Benzamide gave, as the only product, meta-nitrobenzamide; phenylacetamide gave paranitrophenylacetamide, melting at 191° , and phenylpropionamide gave the *paranitro*-derivative, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$; this crystallises from its hot aqueous

solution in light, glistening needles, melting at $174-175^{\circ}$, is readily soluble in ether or alcohol, and dissolves but sparingly in benzene or chloroform.

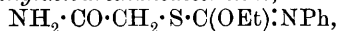
J. J. S.

The So-called Phenylhydantoic Acids. By RIZZO NICCOLÒ (*Gazzetta*, 1898, 28, i, 356—370).—The substance obtained by Jäger (*J. pr. Chem.*, 1877, [ii], 16, 17, 29) from aniline, ammonium thiocyanate and chloracetic acid is not a phenylhydantoic acid but a carbamine-thioglycollanilide, $\text{NH}_2\cdot\text{CO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$; contrary to Jäger's statement, it is hydrolysed by water, yielding ammonia, carbonic anhydride, and *thioglycollanilide*, $\text{SH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$. The latter crystallises in needles melting at $106-107^{\circ}$, has the normal molecular weight in freezing acetic acid, and is soluble in water and organic solvents; it must be prepared in an atmosphere of hydrogen sulphide, because its solution oxidises in the air, yielding *dithiodiglycollanilide*, $\text{S}_2(\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_2$, which melts at 165° .

Thiodiglycollanilide, $(\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2)_2\text{S}$, obtained by passing a current of hydrogen sulphide through a solution of chloracetanilide in alcoholic ammonia, crystallises in white needles melting at $160-161^{\circ}$; it is insoluble in water, and has the normal molecular weight in boiling benzene or acetic acid.

On treating thioglycollanilide or carbaminethioglycollanilide with sodium methoxide and methylic iodide, *methylothioglycollanilide*, $\text{SMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, is obtained; it crystallises in needles melting at 80° , or in scales melting at 76° . On boiling carbaminethioglycollanilide with aniline, the symmetrical diphenylcarbamide melting at 235° is produced.

On heating a solution of chloracetamide, phenylthiourethane, and soda in much alcohol, *phenylthiourethaneacetamide*,



is obtained; it crystallises in colourless needles and melts at $93-94^{\circ}$. This substance could not be converted into an isomeride of Jäger's compound, but yields phenylthiocarbamide glycollide, $\text{CO}\begin{matrix} \text{NPh}\cdot\text{CO} \\ | \\ \text{S}-\text{CH}_2 \end{matrix}$, on hydrolysis.

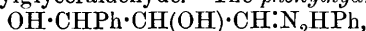
On boiling ammonium thiocarbamate with chloracetanilide in alcoholic solution, thiodiglycollanilide is obtained; the same compound is produced on boiling chloracetanilide and xanthogenamide with soda in alcoholic solution. Barium or ammonium thiocyanate reacts with chloracetanilide and soda in alcoholic solution, yielding thiocyanacetanilide; attempts to synthesise Jäger's compound from this substance were also unsuccessful.

W. J. P.

Some Aromatic Acetals and Aldehydes. By EMIL FISCHER and ERWIN HOFFA (*Ber.*, 1898, 31, 1989—1998. Compare this vol., i, 311).—Aromatic aldehydes of the type of benzaldehyde give only a small yield of an acetal when treated with dilute alcoholic hydrogen chloride, unless a strongly negative group is present in the nucleus. Aldehydes in which the aldehyde group is not directly united with the aromatic nucleus, on the other hand, can be converted in this way into acetals almost as readily as the fatty aldehydes. *Phenylacetaldehyde dimethylacetal*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OMe})_2$, is readily formed by the action

of methylic alcohol containing 1 per cent. of hydrogen chloride on phenylacetaldehyde. It boils at $219\text{--}221^\circ$ (corr.), has a specific gravity = 1.0042 at 18° , and does not possess a characteristic odour.

Cinnamaldehydedimethylacetal, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{OMe})_2$, has been previously described, and has also been prepared by Claisen by the aid of formimidoether (this vol., i, 421). It is converted by reduction with sodium and alcohol into *hydrocinnamaldehydedimethylacetal*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})_2$, which is, however, best prepared in a pure state from hydrocinnamaldehyde, and then boils at $240\text{--}241^\circ$ (corr.), undergoing a very slight amount of decomposition. Hydrocinnamaldehyde is obtained by the hydrolysis of the crude acetal, and has also been prepared by von Miller and Rohde (Abstr., 1890, 979); it boils at $104\text{--}105^\circ$ (corr.) under a pressure of 13 mm. The aldehyde undergoes condensation with acetaldehyde in presence of aqueous soda forming *phenopentenal*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$; this boils at $138\text{--}139^\circ$ (corr.) under a pressure of 13 mm., and shows the ordinary aldehyde reactions. On exposure to the air, it yields an acid melting at 102.5° (corr.), which is probably phenyl- $\alpha\beta$ -pentoic acid. The *phenylhydrazone* crystallises in soft needles melting at about 100° , whilst the *oxime* crystallises in prisms melting at 109° (corr.). Cinnam-acetal is converted by alkaline potassium permanganate into *phenylglyceraldehydedimethylacetal*, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OMe})_2$, which crystallises in rhomboidal tablets melting at $79\text{--}80^\circ$ (corr.); this is sparingly soluble in cold water, and does not reduce Fehling's solution even on boiling. The acetal is very readily hydrolysed by very dilute acids, yielding a solution which reduces Fehling's solution in the cold, and contains phenylglyceraldehyde. The *phenylhydrazone*,



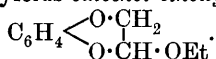
which crystallises out when phenylhydrazine acetate is added to the solution of the aldehyde, forms long, pointed prisms, which melt at 170.5° (corr.). The *sodium hydrogen sulphite* compound crystallises in colourless needles, and is very sparingly soluble in concentrated sodium hydrogen sulphite solution.

When the acetal is hydrolysed with 1 per cent. sulphuric acid, an oil separates which appears to be a polymeride of phenylglyceraldehyde; it solidifies after a time, and then crystallises from alcohol in lustrous leaflets which melt at $114\text{--}125^\circ$, and could not be obtained pure and of constant composition and melting point; with phenylhydrazine, its alcoholic solution yields the hydrazone described above, and it can be reconverted into the acetal in the usual way. Phenylglyceraldehyde may be regarded as the next lower homologue of phenyltetrose.

A. H.

Acetals Derived from Catechol. By CHARLES MOUREU (*Compt. rend.*, 1898, 126, 1656—1658).—When catechol is heated in a sealed tube at 175° with monochloroacetal and absolute alcohol, *phenoloxyacetal*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, is formed, together with a certain proportion of *phenylenedioxydiacetal*, $\text{C}_6\text{H}_4[\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2]_2$. The latter remains undissolved when the product of the reaction is treated with dilute soda, whilst the alkaline solution, on acidification with hydrochloric acid, yields phenoloxyacetal as a heavy, insoluble oil,

which decomposes on distillation, even under diminished pressure. On boiling with dilute sulphuric acid, it is converted into the corresponding *aldehyde*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHO}$, which is a heavy, oily liquid, boiling without decomposition at 139° under a pressure of 9 mm. This substance is soluble in alkalis, and is reprecipitated on the addition of acids to its solutions; it forms a crystalline compound with sodium hydrogen sulphite, and gives the general reactions of aldehydes, but yields no coloration with ferric chloride, although containing phenolic hydroxyl. When heated to 225° , it loses water, and is probably converted into acetylene catechol, which then undergoes polymerisation or oxidation. The *acetate*, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHO}$, boils without decomposition at 141° under a pressure of 8 mm., and decomposes at about 220° . Phenoxylacetal, when heated to 210 – 215° , loses a molecule of alcohol, and yields *catechol ethoxyethylenic ether*,



This is a colourless oil boiling at 247° (corr.) and having a sp. gr. = 1.158 at 0° ; on boiling with dilute sulphuric acid, a second molecule of alcohol is eliminated, with formation of the aldehyde previously described.

Phenylenedioxydiacetal is an oily liquid boiling at 195 – 197° under a pressure of 9 mm., and having a sp. gr. = 1.061 at 0° ; by dilute sulphuric acid, it is hydrolysed to the corresponding aldehyde, which is soluble in water, and slightly soluble in ether. N. L.

Derivatives of Vanillin. By ALBERT E. MENKE and WILLIAM B. BENTLEY (*J. Amer. Chem. Soc.*, 1898, 20, 316–317).—*Chlorovanillin*, obtained by the action of chlorine on vanillin dissolved in chloroform, melts at 166° , and, on reduction with sodium amalgam, gives rise to *chlorovanilloin*, which melts at 255° . A *chloroprotocatechuic acid*, melting at about 235° , appears to be formed when chlorovanillin is fused with potassium hydroxide. On passing chlorine into an alcoholic solution of protocatechuic acid, a resinous substance was formed, from which, by treatment with caustic potash, tetrachlorocatechol was obtained.

The action of dilute nitric acid on vanillin, gives rise to dinitroguaiacol, together with two other *substances*; the first of these is colourless, insoluble in the usual solvents, and melts at about 300° ; the second is yellow, melts at 178 – 179° , is soluble in alcohol, and is either nitrovanillin or an additive compound of this and dinitroguaiacol; with nitric acid, it gives rise to dinitroguaiacol, and on oxidation with potassium permanganate, *nitrovanillic acid*, which melts at 214° , is obtained. W. A. D.

Halogen Derivatives of Phenyl Ethyl Ketone. By A. COLLET (*Compt. rend.*, 1898, 126, 1577–1579).—The compounds described in this paper were obtained by the action of propionic chloride or α -bromopropionic chloride on chlorobenzene or bromobenzene in presence of aluminium chloride. *Parachlorophenyl ethyl ketone*, which forms small, colourless crystals, melts at about 35 – 36° , and is soluble in alcohol or carbon bisulphide. When oxidised with alkaline per-

manganate, it yields parachlorobenzoic acid. Its *oxime* forms nacreous lamellæ, which melt at 62—62·5°, whilst the *phenylhydrazone* crystallises in colourless needles which melt at 94—96°. *Parabromophenyl ethyl ketone*, which forms brilliant, colourless needles, melts at 44—45°, and yields parabromobenzoic acid on oxidation. Its *oxime* melts at 90—91°, and its *phenylhydrazone* at 99—101°; both crystallise in needles. *Parachlorophenyl bromethyl ketone* forms brilliant crystals, which melt at 77·5°; it yields parachlorobenzoic acid when oxidised. The *anilide*, $\text{NHPh} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl}$, forms yellow needles, which melt at 111—111·5°. Parabromophenyl bromethyl ketone forms brilliant, colourless lamellæ which melt at 84—84·5°; its vapour, and that of the preceding ketone, are very irritating to the eyes. The *anilide* crystallises in yellow scales, which melt at 109·5—110° (compare this vol., i, 139).
C. H. B.

Allocinnamic Acid. By CARL LIEBERMANN (*Ber.*, 1898, 31, 2095—2098).—When allocinnamic acid is triturated with fuming sulphuric acid, truxone is produced, together with a small quantity of a bye-product which develops a violet coloration when warmed with potash. This impurity is removed by treatment with chromic acid, and the truxone thus obtained appears to be more soluble in hot glacial acetic acid than that produced from α -truxillic acid (*Abstr.*, 1889, 699), but a mixture of the two gives the same melting point, 294—295°, as either of these preparations. When treated with sulphuric acid, cinnamic acid only yields a trace of truxone. This ready formation of indones lends additional support to the space formula, $\begin{array}{c} \text{Ph} \cdot \text{C} \cdot \text{H} \\ | \\ \text{COOH} \cdot \text{C} \cdot \text{H} \end{array}$, for the allocinnamic acid series, and serves to

identify these compounds. On treating a mixture of α - and β -dibromocinnamic acids with sulphuric acid, the latter alone is converted into dibromindone, whilst the former remains unaltered.

When Glaser's monobromocinnamic acids are similarly treated, the so-called β -acid (α -bromallocinnamic acid) alone yields an anhydro-compound, to which Leukart gave the formula $\text{C}_{17}\text{H}_{12}\text{Br}_2\text{O}_2$, but which may be a monobromotruxone $(\text{C}_9\text{H}_5\text{BrO})_x$ (*Abstr.*, 1882, 615). The author is unable to corroborate Erlenmeyer's observation (*Abstr.*, 1896, i, 46) that allocinnamic acid, when dissolved in alcohol containing zinc bromide, changes into isocinnamic acid. Solutions of pure allocinnamic acid, after remaining for several months, showed no trace of any change; moreover, allocinnamic acid, its aniline salt, and allocinnamylidenecetic acid were found to have undergone no change after keeping for several years.
G. T. M.

Phenyl- $\gamma\delta$ -pentenoic Acid. By FRITZ FICHTER and ALEXANDER BAUER (*Ber.*, 1898, 31, 2001—2004. Compare *Abstr.*, 1897, i, 13 and 590).—*Ethyl benzoylglutarate*, $\text{COOEt} \cdot \text{CH}(\text{COPh}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOEt}$, synthesised from ethylic sodiobenzoylacetate and ethylic β -iodopropionate, is a colourless liquid boiling at 200—210° under a pressure of 12 mm. On acidic hydrolysis, it gives rise to benzoic and glutaric acids, whilst the ketonic hydrolysis yields γ -benzoylbutyric acid.

δ -Phenyl- δ -valerolactone- γ -carboxylic acid, $\text{COOH} \cdot \text{CH} \begin{array}{c} \text{CHPh} \cdot \text{O} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CO}$,

obtained by reducing the preceding compound with sodium amalgam in dilute alcoholic solution, and subsequently heating the product of reduction in a current of dry air at 125° , crystallises from ether and light petroleum in small, white nodules, and melts at 161° .

Phenyl- $\gamma\delta$ -pentenoic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, produced either by distilling the above lactone, or by boiling its aqueous solution for some hours, crystallises from light petroleum in shining leaflets, melts at $90\text{--}91^{\circ}$, and is soluble in ether, carbon bisulphide, chloroform, and hot water. Its melting point and the properties of its salts (the *calcium*, *barium*, and *silver* salts are described) distinguish it from its $\beta\gamma$ - and $\alpha\beta$ -isomerides (Abstr., 1880, 407, and 1895, i, 223). Like other $\gamma\delta$ -unsaturated acids, it is neither reduced by sodium amalgam nor acted on by caustic soda; hydriodic acid reduces it to normal phenylvaleric acid.

$\gamma\delta$ -Dibromophenylvaleric acid is obtained by the action of bromine on the $\gamma\delta$ -unsaturated acid; it crystallises from light petroleum in colourless needles and melts at 162° . A phenylbromovaleric acid results from the addition of hydrogen bromide to the $\gamma\delta$ -acid, which, although having the same melting point as Perrin's γ -bromophenylvaleric acid (Abstr., 1895, i, 224), differs from it in being reconverted into phenyl- $\gamma\delta$ -pentenoic acid when boiled with water or digested with sodium carbonate; Perrin's acid, under these conditions, yields phenylvalerolactone.

Benzylideneglutaric acid (Abstr., 1895, i, 141) is produced in small amount by the distillation of δ -phenyl- δ -valerolactonecarboxylic acid in the preparation of phenyl- $\gamma\delta$ -pentenoic acid. G. T. M.

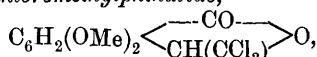
Products of the Iodisation of Aromatic Alcohols, Aldehydes, and Acids. By JOHANNES SEIDEL (*J. pr. Chem.*, 1898, [ii], 57, 495—496. Compare this vol., i, 367).—When moniodanisaldehyde is boiled with alcoholic potash, it yields 3-iodanisic acid, and a moniodanisyl alcohol melting at 84° ; the *phenylhydrazone* melts at $106\cdot5\text{--}107^{\circ}$, the *oxime* at $129\text{--}130^{\circ}$, the *anil* at $107\text{--}108^{\circ}$.

3-Iodanisic acid, when heated at $150\text{--}160^{\circ}$ in the presence of iodine, yields 2:4-di-iodanisole, melting at $65\cdot5\text{--}66\cdot5^{\circ}$. The *methyl*ic salt of the acid melts at 95° , the *ethyl*ic salt rather above 65° .

By iodating coumarin, two products are obtained which are very difficult to purify, as they show no tendency to crystallise. Probably they are derivatives of coumaric acid. A *moniodocoumarin* melting at $164\text{--}165^{\circ}$ and a *di-iodocoumarin* melting at 192° were obtained, however, from the corresponding iodine derivatives of salicylaldehyde by the Perkin reaction. C. F. B.

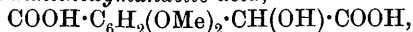
Condensation of Chloral with Methyl 2:3-Dimethoxybenzoate: Synthesis of Meconine. By PAUL FRITSCH (*Annalen*, 1898, 301, 352—361. Compare Abstr., 1897, i, 568).—Guaiacolcarboxylic acid separates from water in crystals containing $1\text{H}_2\text{O}$, and melts at 152° ; the *methyl*ic salt crystallises from methyl alcohol in aggregates of needles and melts at 63° . *Methyl 2:3-dimethoxybenzoate* $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{COOMe}$, is deposited from the ethereal solution in lustrous plates, and melts at 47° ; it boils at $184\text{--}185^{\circ}$ under a pressure of 50 mm.

5 : 6-Dimethoxytrichloromethylphthalide,



obtained by the condensation of methylic 2 : 3-dimethoxybenzoate with chloral under the influence of concentrated sulphuric acid, crystallises from alcohol in stellate aggregates of needles, and melts at 104°.

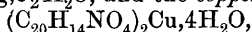
2-Carboxy-3 : 4-dimethoxymandelic acid,



prepared by hydrolysing the foregoing substance with 20 per cent. caustic soda at 50°, separates from water in crystals containing 1H₂O ; it crystallises from wet ethylic acetate in needles containing 2H₂O, and chars when heated. The *barium* salt crystallises in slender needles containing 4H₂O. When the acid is heated in small quantities, meconine distils from the charred product. M. O. F.

Action of Phthalic Anhydride on Para- and Meta-hydroxydiphenylamine. By ARNALDO PIUTTI and R. PICCOLI (*Gazzetta*, 1898, 28, i, 370—382).—Piutti has previously shown (Abstr., 1884, 448) that phthalic anhydride reacts with secondary monamines yielding disubstituted phthalamic acids or tetra-substituted asymmetric phthalic diamides ; the production of the rhodamines by condensing phthalic anhydride with amidophenols is now a commercial process.

On heating phthalic anhydride with parahydroxydiphenylamine, in molecular proportion, at 195°, *parahydroxydiphenylphthalamic acid*, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is obtained ; it crystallises in colourless prisms melting at 191—192°, and is insoluble in water. The *silver* salt, $\text{C}_{20}\text{H}_{14}\text{NO}_4\text{Ag} \cdot 3\frac{1}{2}\text{H}_2\text{O}$, and the *copper* salt,

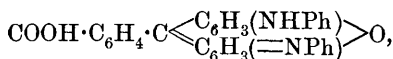


were prepared ; the *ethylic* salt, $\text{C}_{20}\text{H}_{14}\text{NO}_4\text{Et}$, crystallises in needles melting at 166—168°. The *methoxy*-derivative, $\text{C}_{21}\text{H}_{17}\text{NO}_4$, prepared by the aid of methylic iodide and potash, is amorphous and melts at 90—92°. *Parethoxydiphenylphthalamic acid*, $\text{C}_{22}\text{H}_{19}\text{NO}_4$, is also amorphous and melts at 80—82° ; the *silver* salts of both these acids were analysed. The benzoyl and acetyl derivatives of the hydroxy-acid melt below 100°, but are not well-defined.

No well-defined new compound could be isolated from the product of the reaction of two molecular proportions of the amine with one of anhydride.

Metahydroxydiphenylamine and phthalic anhydride react in molecular proportion with production of *metahydroxydiphenylphthalamic acid*, $\text{C}_{20}\text{H}_{15}\text{NO}_4$, which forms white, crystalline crusts melting at 191—192° ; it readily yields rhodamines when heated with dehydrating agents, and its *silver* salt is anhydrous and crystalline. The *ethylic* salt forms crystalline crusts melting at 155—157°. The *methoxy*-derivative of the acid, $\text{C}_{21}\text{H}_{17}\text{NO}_4$, is very soluble in organic solvents and melts at 95—98° the corresponding *ethoxy*-derivative is similar and melts at 88—90°. The *silver* salts of both acids were analysed, but the benzoyl and acetyl derivatives of the hydroxy-acid are, again, not characteristic.

On heating metahydroxydiphenylamine (2 mols.) with phthalic anhydride (1 mol.) at 160°, the diphenylrhodamine,



melting at 260—262° is obtained; its solutions in benzene and carbon bisulphide are colourless.

W. J. P.

Propylphthalide and its Hydrolysis by Caustic Alkalis. By PIETRO GUCCI (*Gazzetta*, 1898, 28, i, 297—304).—On heating a mixture of phthalic anhydride, zinc dust, and normal propylic iodide, much gas is evolved, and the residue, when distilled in a current of steam, yields *propylphthalide*, $\text{C}_6\text{H}_4 \begin{array}{l} \swarrow \text{CHPr} \\ \searrow \text{CO} \end{array} \text{O}$, as an oil which boils at 243—247° under 220 mm. pressure and at 293—297° under 735 mm. pressure. When heated, it yields propylene and phthalide, and when fused with soda gives benzoic acid and butyraldehyde. Its odour resembles that of sedanolide, a tetrahydrobutylphthalide extracted from oil of celery by Ciamician and Silber. The monalkyl phthalides possess an odour of celery which is independent of the degree of hydrogenation of the aromatic nucleus.

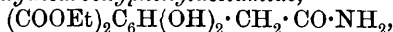
W. J. P.

New Method of Preparing Ethylic Orcintricarboxylate [Dihydroxydicarboxyphenylacetate]. By HANS VON PECHMANN and LUDWIG WOLMAN (*Ber.*, 1898, 31, 2014—2017. Compare *Abstr.*, 1886, 802).—If in the preparation of ethylic acetonedicarboxylate the alcoholic solution of ethylic acetonedicarboxylic acid saturated with hydrogen chloride is allowed to remain for 2 or 3 weeks, a considerable yield of ethylic orcintricarboxylate (dihydroxydicarboxyphenylacetate) is obtained.

The diethylic salt, $(\text{COOEt})_2\text{C}_6\text{H}(\text{OH})_2 \cdot \text{CH}_2 \cdot \text{COOH}$, produced from the preceding compound on hydrolysis with dilute alkali in the cold, crystallises from alcohol in rhombohedra, melts at 183—184°, and is soluble in alcohol, acetone, chloroform, and hot water. It gives the homofluorescein reaction with chloroform and caustic soda, and is coloured red by ferric chloride.

Dihydroxyphenylacetic acid is obtained by the hydrolysis of the preceding compound with the aid of heat, and is isolated by means of its *lead* salt, $(\text{C}_8\text{H}_7\text{O}_4)_2\text{Pb} + 2\text{H}_2\text{O}$; when obtained by evaporating its aqueous solution to dryness, the acid melts at 127—128°, but if allowed to crystallise spontaneously, its melting point is 54°; doubtless this is due to difference in the amount of water of crystallisation in the two cases.

Ethylic dihydroxydicarboxyphenylacetamide,



obtained on treating an alcoholic solution of ethylic orcintricarboxylate with concentrated ammonia, crystallises from alcohol in slender needles, and melts at 186°; it is sparingly soluble in the ordinary solvents, dissolving most readily in chloroform and acetone. Its *monosodium* salt crystallises from alcohol in prisms, and is decomposed by water.

Dihydroxydicarboxyphenylacetamide, produced from the above amide by digestion with cold caustic soda, crystallises from alcohol in prisms and melts at 221—222°.

G. T. M.

Derivatives of Benzenesulphonic Acid. By THOMAS H. NORTON (*J. Amer. Chem. Soc.*, 1897, 19, 835—838).—Benzenesulphonic bromide can readily be prepared by treating sodium benzenesulphonate with phosphorus pentabromide, about one-fourth of the theoretical yield being obtained. *Sodium benzenesulphonate* crystallises in small, white leaflets, and melts at about 450°; the *potassium* salt forms long, colourless needles and melts at about 408°, whilst the *ammonium* salt is deliquescent, and melts and decomposes at 256°; the *lithium* salt crystallises in stellate groups of white needles and melts at a dull red heat.

A. H.

Hydroxysulphonic Acids and Sultones. By WILHELM MARCOWALD and H. H. FRAHNE (*Ber.*, 1898, 31, 1854—1865).—Orthonitrobenzylic chloride was converted into *orthonitrobenzylsulphonic acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, by boiling it with a saturated aqueous solution of sodium sulphite; this acid forms hygroscopic crystals; the *sodium*, *barium*, and *silver* salts crystallise with 1, 3 (of which only 2 are lost at 100°), and $1\text{H}_2\text{O}$, respectively. When reduced with iron and acetic acid, the acid is converted into *orthamidobenzylsulphonic acid*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, a crystalline substance, the *sodium* salt of which crystallises with $1\text{H}_2\text{O}$. When this salt and sodium nitrite are dissolved in water, and dilute sulphuric acid added to the well cooled mixture, which is then warmed on the water bath, *benzylsultone*, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{SO}_2$, is formed. This melts at 86°, and is not affected by alkalis in the cold, but when boiled with them, it yields salts of *orthohydroxybenzylsulphonic acid*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, itself a syrupy liquid; the *barium* salt crystallises with $4\text{H}_2\text{O}$, the *lead* salt with $7\text{H}_2\text{O}$; the *ammonium* salt is anhydrous; from the acid, the sultone is not easily regenerated, but the transformation can be effected by the action of phosphorus pentachloride. The sultone, on warming with bromine in chloroform solution, yields *monobromobenzylsultone* [$\text{CH}_2 : \text{O} : \text{Br} = 1 : 2 : 5$, probably], which melts at 147°; with fuming nitric acid and sulphuric acid, it yields *mononitrobenzylsultone*, melting at 148°, and this is converted into *nitrohydroxybenzylsulphonic acid*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, when it is boiled with water for a long time; this acid forms hygroscopic crystals, and yields a *mono-* and a *di-potassium* salt, the latter crystallising with $1\text{H}_2\text{O}$, whilst with ammonia it forms, not the ammonium salt, but *nitro-orthohydroxybenzylsulphonamide*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{SO}_2 \cdot \text{NH}_2$; this amide melts and decomposes at 199°, and has pronounced acid properties; its *potassium* and *silver* derivatives were prepared, and from the latter and methylic iodide, *nitro-orthomethoxybenzylsulphonamide*, melting at about 100°, was obtained. Nitrobenzylsultone can be reduced with tin and hydrochloric acid to *amidobenzylsultone*, $\text{NH}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{SO}_2$, which melts at 138°; the *hydrochloride*, and the yellow *picrate*, the latter melting and decomposing at about 170°, were prepared; the base, when diazotised, forms *orthohydroxydiazobenzylsulphonic acid*, $\text{OH} \cdot \text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{SO}_2 \cdot \text{N} \cdot \text{N} \cdot \text{O}$, which was obtained impure as a syrup.

γ -Hydroxypropanesulphonic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, can be obtained quite readily by boiling allylic alcohol with a strong solution of potassium hydrogen sulphite, and also by reducing acraldehydesulphonic acid, $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ (Rosenthal, Abstr., 1886, 866), with potassium amalgam. It cannot be made to yield a sulfone.

C. F. B.

Synthesis of Safranine. By GEORGE F. JAUBERT (*Compt. rend.*, 1898, 126, 1515—1518).—*Trinitrophenosafranine* is obtained by oxidising a mixture of trinitrophenylmetaphenylenediamine with paraphenylenediamine, in molecular proportion, in acetic acid solution, and boiling the alcoholic solution of the indamine thus obtained; it has considerable tinctorial power, and dyes ruby-red on cotton mordanted with tannin or tartar emetic. The trinitrophenylmetaphenylenediamine, prepared by the action of picryl chloride on metaphenylenediamine hydrochloride in presence of alcohol and dry sodium acetate, crystallises from acetone in orange prisms, melts at 207° , and is only slightly soluble in alcohol or acetic acid, but readily in solutions of alkali hydroxides.

Trinitrodimethylphenosafranine is obtained by the action of nitrosodimethylaniline on trinitrophenylmetaphenylenediamine, or by the oxidation of a mixture of paraphenylenediamine and trinitrophenyldimethylmetaphenylenediamine, in molecular proportion, the indamine thus obtained being boiled with alcohol. It forms green needles, and dyes a very fast red-violet on cotton mordanted with tannin or with tartar emetic. Trinitrophenyldimethylmetaphenylenediamine can be obtained by the action of picryl chloride on metamidodimethylaniline hydrochloride in presence of alcohol and dry sodium acetate; it forms red crystals.

Since, in these cases, there is double substitution in the ortho-position relatively to the nitrogen in the phenylic group, the formation of the safranines would be impossible if their constitution were represented by Nietzki's asymmetrical formula, and the author regards the formation of the compounds described in this paper as additional proof of the validity of his symmetrical formula for safranines (this vol., i, 494).

C. H. B.

Dibenzylidenediethyl Ketone. By DANIEL VORLÄNDER and F. WILCKE (*Ber.*, 1898, 31, 1886—1888).—When the compound $\text{CO}\begin{matrix} \text{CHMe}\cdot\text{CHPh} \\ \text{CHMe}\cdot\text{CHPh} \end{matrix}\text{O}$ (Abstr., 1896, i, 546, 603) is dissolved in acetic acid, dry hydrogen chloride gas passed into the boiling solution for 2 hours, and then into the cooled solution to saturation, the solution being finally allowed to remain for 4 days, *dibenzylidenediethyl ketone*, $\text{CO}(\text{CMe}\cdot\text{CHPh})_2$, is precipitated when the product is poured into water. This ketone melts at 122° , is not decomposed by boiling hydrochloric acid, unites with bromine in chloroform solution, although but slowly, to form a *tetrabromide*, which decomposes and melts at about 180° , and forms an *oxime* which melts at 157 — 159° .

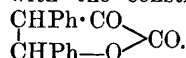
C. F. B.

Oxylactones—Ketolactones. By EMIL ERLENMEYER, jun., and MICHAEL LUX (*Ber.*, 1898, 31, 2218—2224. Compare Erlenmeyer and Knight, Abstr., 1894, i, 592).—The *benzyl* derivative of α -oxy-

β -phenyl- γ -benzylbutyrolactone is obtained when the lactone (10 grams) and sodium (0.88 gram) are separately dissolved in absolute alcohol and then mixed and boiled with benzylic chloride for 6 hours, or until the solution is neutral. When recrystallised from alcohol, it forms large prisms melting at 67° , sparingly soluble in water, but readily in the usual organic solvents. The *benzoyl* derivative, $C_{24}H_{18}O_4$, readily obtained by the Schotten-Baumann method, crystallises from alcohol in colourless plates melting at 137° , and gives no coloration with ferric chloride.

A better yield of α -oxy- $\beta\gamma$ -diphenylbutyrolactone (Abstr., 1894, i, 592) is obtained by suspending ethylic phenylcyanopyruvic acid in concentrated hydrochloric acid, mixing with the requisite quantity of benzaldehyde, and allowing the mixture to remain at the ordinary temperature for 14 days, with occasional shaking; from 10 grams of the ethylic salt, 10 grams of the lactone may be obtained. The *benzoyl* derivative, $C_{23}H_{16}O_4$, crystallises from its alcoholic solution in needles melting at 137° ; it is insoluble in water, and is not coloured by ferric chloride.

When the lactone is distilled, a copious evolution of gas occurs, and stilbene is formed, a reaction which is completely in accordance with the constitution of the lactone previously given, namely,



J. J. S.

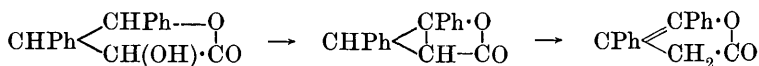
Conversion of an $\alpha\gamma$ -Dihydroxy-acid into the Corresponding Ketone. By EMIL ERLÉNMEYER, jun., and MICHAEL LUX (*Ber.*, 1898, 31, 2224—2238).—When α -oxy- $\beta\gamma$ -diphenylbutyrolactone (compare preceding abstract) is suspended in water, reduced with 4 per cent. sodium amalgam, and the solution neutralised from time to time with hydrochloric acid, a mixture of two *stereoisomeric hydroxylactones*,

$\text{CHPh} \begin{cases} \text{CHPh} - \text{O} \\ \text{CH(OH)} \cdot \text{CO} \end{cases}$, is obtained. The mixture, which is at first syrupy, may be purified by dissolving it in chloroform and adding light petroleum, when colourless needles melting at 127° separate. The hydrochloric acid solution also yields the same two compounds, namely, the one melting at 127° and a second at 170° . Both compounds are sparingly soluble in water, ether, or light petroleum, but dissolve readily in warm alcohol, benzene, or chloroform. Phenyl- α -lactic acid may also be isolated from the products of reduction; it is probably formed by the decomposition of the oxylactone into phenylpyruvic acid and benzaldehyde, and the subsequent reduction of the phenylpyruvic acid.

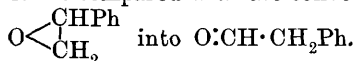
They are both readily hydrolysed to the *corresponding dihydroxy-acids* by sodium hydroxide, and as the sodium salt derived from the lactone melting at 127° is much more sparingly soluble than the isomeric salt, this affords a convenient method of separating the two compounds. The *silver* salts of the two hydroxy-acids have been prepared and analysed. When the reduction of the oxylactone is brought about by the aid of zinc dust and acetic acid, the products are desylacetic acid, diphenylcrotonolactone, previously obtained by Klingemann (Abstr., 1892, 1002) by heating desylacetic acid, and finally an

acid, $C_{16}H_{14}O_3$, isomeric with desylacetic acid and with the two hydroxylactones. This acid is found as its zinc salt mixed with the zinc which has not been acted on and the zinc acetate; it is sparingly soluble in cold water or light petroleum, but dissolves readily in the usual organic solvents, and its alcoholic solution gives no coloration with ferric chloride. Its *methylic* salt, $C_{15}H_{13}O \cdot COOMe$, crystallises from hot light petroleum in glistening needles melting at 89° ; it is readily soluble in ether, alcohol, benzene, chloroform or carbon bisulphide, but is only sparingly soluble in water or light petroleum. The acid combines with bromine, yielding a solid product from which two compounds may be obtained by crystallisation from a mixture of chloroform and light petroleum; the one crystallises in quadratic plates decomposing at 140 — 144° and the other in colourless needles turning brown at 90° and decomposing at 105° .

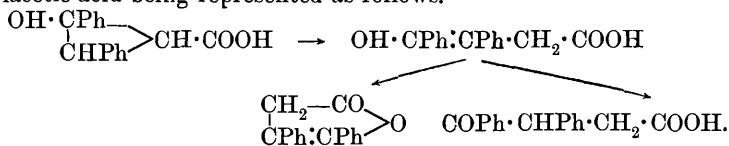
When the acid, $C_{16}H_{14}O_3$, is heated with dilute acetic or hydrochloric acid, it is converted into diphenylcrotonolactone, and this in its turn into desylacetic acid. The two hydroxylactones (melting at 127° and 170° respectively) behave with acetic or hydrochloric acid in an exactly similar manner. The conversion of the hydroxylactone into the unsaturated lactone seems to be brought about as follows.



the last stage of which is compared with the conversion of

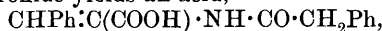


For the acid $C_{16}H_{14}O_3$, the constitution $\begin{array}{c} OH \cdot CPh- \\ | \\ CHPh \end{array} > CH \cdot COOH$ is suggested, the conversion of this acid into diphenylcrotonolactone and desylacetic acid being represented as follows.



J. J. S.

Remarkable Conversion of an α -Ketonic Acid into the Corresponding α -Amido-acid. By EMIL ERLLENMEYER, jun. (*Ber.*, 1898, 31, 2238—2240).—By the condensation of phenaceturic acid with benzaldehyde, a compound, $\begin{array}{c} CHPh:C \\ | \\ CH_2Ph \cdot CO \cdot N \end{array} > CO$, is obtained; it is a pale yellow substance with neutral properties, and when warmed with sodium hydroxide yields an acid,



which crystallises well and yields a somewhat sparingly soluble sodium salt. When dissolved in sodium carbonate and reduced with 4 per cent. sodium amalgam while a current of carbonic anhydride is passed through the liquid, this acid yields another acid, $C_{17}H_{17}NO_3$, melting at 126° and identical with that obtained from phenylpyruvic acid

(this vol., i, 197), so that the constitution previously given is established.

J. J. S.

Dialkylamido-orthobenzoylbenzoic and Dialkylamido-orthobenzylbenzoic Acids. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1898, **126**, 1248—1251).—The crystals of dimethylamido-orthobenzoylbenzoic acid which melt at 199° , are hydrated, and effloresce readily; they become anhydrous at 120° , and then melt at 203 — 204° (uncorr.). The acid also crystallises with methylic alcohol, but forms no similar compound with propylic and butylic alcohols. The magnesium salt, with $6\text{H}_2\text{O}$, crystallises in large, pale yellow crystals; the barium salt, with $2\text{H}_2\text{O}$, in pale yellow, prismatic needles; the platinochloride, with $2\text{H}_2\text{O}$, in transparent, orange prisms. When the barium salt is heated, it yields a dimethylparamidobenzophenone, melting at 92° and identical with Doebner's benzodimethylaniline.

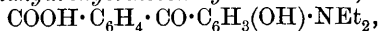
The phenylhydrazine compound of the acid, which is derived from equal molecular proportions of its two components, forms colourless needles melting at 158° . From benzene, it crystallises in large, brilliant prisms which contain benzene and effloresce rapidly.

When the acid is suspended in water and treated with sodium amalgam, it yields dimethylamidomonophenylphthalide, which crystallises from chloroform in nacreous leaflets melting at 188° . It has been obtained by Ebert (*Abstr.*, 1896, i, 441), and by Limpricht.

Dimethylamidobenzylbenzoic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, obtained by the prolonged action of sodium amalgam, or, better, by the action of zinc powder and potassium hydroxide, melts at 174° , and crystallises from acetic acid or alcohol in large prisms or leaflets. Its methylic salt crystallises in large, colourless, transparent prisms, which melt at 62° , and can be distilled without decomposing. When dissolved in acetic acid and mixed with lead peroxide, it gives an intense violet coloration.

Diethylamidobenzoylbenzoic acid crystallises from methylic or ethylic alcohol in large prisms containing one molecular proportion of the alcohol; the anhydrous acid melts at 180° . When heated with diethylaniline in presence of acetic anhydride or phosphorus trichloride, it yields diethylanilinephthalein, which crystallises in leaflets or needles melting at 128° . With sodium amalgam, the acid yields a phthalide, and with zinc powder and sodium hydroxide, it yields diethylamidobenzylbenzoic acid melting at 108° .

Diethylamidometahydroxyorthobenzoylbenzoic acid,



forms slender, white needles, which melt and decompose at 203° ; it is obtained by the condensation of phthalic anhydride and diethylamido-resorcinol, in molecular proportion. When reduced with zinc powder and potassium hydroxide solution, it yields *diethylamidometahydroxybenzylbenzoic acid*, which will be described later.

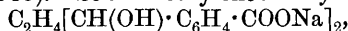
C. H. B.

Phenoxycinnamic [Hydroxyphenylcinnamic] Acid. By ALB. J. J. VAN DE VELDE (*Rec. Trav. Chim.*, 1897, **16**, 287—288, from *Bull. Acad. Roy. Belg.*, 1897, [iii], **33**, 221—229).—*Hydroxyphenylcinnamic acid*, $\text{CHPh}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{COOH}$, is readily obtained when benzaldehyde, sodium hydroxyphenylacetate, and acetic anhydride

are heated at 140—160° during 18 hours; it is best extracted by large quantities of boiling water, and crystallises as the solution cools. It melts at 121°, and dissolves readily in alcohol, ether, benzene, or chloroform. Its *alkali* salts are soluble in both alcohol and water; its *barium*, *calcium*, *lead* and *silver* salts are insoluble; its *aniline* salt melts at 136°, and dissolves readily in organic solvents; its *phenylic* salt melts at 74°.

When reduced with sodium amalgam and water, it yields *hydroxy-diphenylpropionic acid*, $\text{CH}_2\text{Ph} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{COOH}$, melting at 81°.
J. J. S.

Notes. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1898, 31, 1578—1583).—Sodium ethylenebenzhydrylcarboxylate,

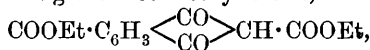


was found some time ago (*Abstr.*, 1878, 428) not to lose water at 200°, although the formation of a substance, $\text{C}_2\text{H}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{COONa})_2$, was expected; it has now been ascertained that, although it loses no water at 212°, at 310° it does lose 1 mol., and yields a product which melts at 208—210°, and appears to be *tetrahydrofuran-dibenzoic acid*, $\text{C}_2\text{H}_4 \langle \text{CH}(\text{C}_6\text{H}_4 \cdot \text{COOH}) \rangle \text{O}$; the *barium*, with $3\text{H}_2\text{O}$, and *silver* salts of this acid were prepared and analysed.

Phenylethylenediamine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NPh}$ (*Abstr.*, 1889, 1166), reacts with benzoin, when the two substances are heated together for three-quarters of an hour at 145—150°, in the same way as ortho-amidoditolyamine, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, does (O. Fischer, *Abstr.*, 1891, 748); the product is 1 : 2 : 3-triphenyltetrahydropyrazine, $\text{N} \langle \text{CH}_2 - \text{CH}_2 \rangle \text{NPh}$, isomeric with that obtained by Garzino (*Abstr.*, 1893, i, 428); it begins to melt at about 110°; its *hydrochloride*, with $2\text{HCl} + \text{H}_2\text{O}$, melts at 224°.

When orthocyanobenzyl cyanide is heated with benzaldehyde and a little piperidine for half an hour at 150°, *ortho-α-dicyanostilbene*, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CN}) \cdot \text{CHPh}$, is formed; it melts at 125·5°. C. F. B.

Diketohydrindenecarboxylic Acid. By FRITZ EPHRAIM (*Ber.*, 1898, 31, 2084—2090).—*Ethylic hemimellithenetricarboxylate*, prepared by treating the silver salt of hemimellithenetricarboxylic acid with ethylic iodide, crystallises from alcohol and ether, and melts at 39°. When ethylic acetate is added to a mixture of this substance and sodium, heated on the water bath, the *sodium* derivative of *diethylic diketohydrindenedicarboxylate* is synthesised; the solution obtained by extracting the mixture with hot water deposits this substance in yellow crystals which contain $1\text{H}_2\text{O}$. The sodium derivative is decomposed by acids, yielding the free diethylic salt,



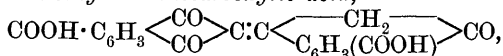
which is precipitated in yellow needles also containing $1\text{H}_2\text{O}$.

The *sodium* derivative of *sodium ethylic diketohydrindenedicarboxylate*, $\text{COONa} \cdot \text{C}_6\text{H}_3 \langle \text{CO} \rangle \text{CNa} \cdot \text{COOEt}$, is also formed in the above reaction, and is obtained from the aqueous extract, after filtering off the above-

mentioned yellow crystals, by saturating it with carbonic anhydride, evaporating to dryness, and extracting the residue with hot alcohol; from this solution, it separates as a pale yellow, crystalline powder. The free acid is unstable.

Both the sodium derivatives, when boiled with acids, lose the carboxyl group attached to the indene ring, by the elimination of carbonic anhydride, but the diketohydrindenecarboxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CH}_2$, and its ethylic salt which should be formed, cannot be isolated owing to the readiness with which they undergo further condensation. The *dioxime* of the latter compound was, however, obtained, $\text{COOEt} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{NOH}) \\ \diagup \quad \diagdown \\ \text{C}(\text{NOH}) \end{smallmatrix} \text{CH}_2$; it crystallises from dilute alcohol in white needles and melts at 186° .

Anhydrobisdiketohydrindenecarboxylic acid,



results from the condensation of diketohydrindenecarboxylic acid in the presence of hydrochloric acid, and can be obtained in dark green flakes; its alkali salts have a reddish-violet colour, and the lead and silver salts form violet precipitates; it is somewhat soluble in water, and dyes unmordanted wool.

Dianhydrobisdiketohydrindenecarboxylic acid, $\text{C}_{20}\text{H}_8\text{O}_6$, obtained by boiling sodium ethylic diketohydrindenecarboxylate with sulphuric acid, is precipitated in green flakes; analysis of its *silver* salt indicates that it is a dibasic acid.

Wislicenus and Reitzenstein noticed that anhydrobisdiketohydrindene underwent further condensation, and that two substances were produced, a red compound which was identified as dianhydrobisdiketohydrindene, and a yellow product which was not obtained pure, and, on further treatment with sulphuric acid, changed into the red compound. The author finds, on the contrary, that the red compound, when suspended in boiling alcohol, is quantitatively converted into the yellow substance which has the same composition, $\text{C}_{36}\text{H}_{16}\text{O}_4$. On heating with aniline, the red dianhydrobisdiketohydrindene readily yields an *anilido*-compound, $\text{C}_{42}\text{H}_{21}\text{O}_3\text{N}$, whereas the yellow substance remains unaltered.

G. T. M.

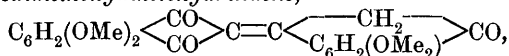
Dimethoxydiketohydrindene and its Derivatives. By JOSEF LANDAU (*Ber.*, 1898, 31, 2090—2094).—Ethylic hemipinate is best prepared by the action of ethylic iodide on the silver salt of hemipinic acid.

The *sodium* derivative of *ethylic dimethoxydiketohydrindenecarboxylate*, $\text{C}_6\text{H}_3(\text{OMe})_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CNa} \cdot \text{COOEt}$, is produced by heating ethylic hemipinate with ethylic acetate and caustic soda at 100° ; the product of reaction, after washing with ether, is dissolved in water, the solution saturated with carbonic anhydride, evaporated to dryness, and the residue extracted in a Soxhlet apparatus with absolute alcohol. The compound separates as a yellow, crystalline powder. On adding acid to a solution of this substance, the *ethylic dimethoxydiketohydrindenecarboxylate*, is obtained in well-defined yellow needles, which decom-

pose at 58° ; it is easily soluble in ether, alcohol, benzene, and acetone, less so in cold water and petroleum; caustic soda regenerates the sodium derivative.

Dimethoxydiketohydrindene, $C_6H_2(OMe)_2 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH_2$, is produced on boiling the preceding compound, or even on digesting it with moist ether; it crystallises from ether or light petroleum in needles having a silvery lustre, melts at $113-115^{\circ}$, and is soluble in the usual solvents; dilute soda dissolves it, forming a sodium derivative.

Anhydrobisdimethoxydiketohydrindene,



is obtained either on heating the preceding compound for some time above its melting point, or on boiling its solution in dilute acids; it crystallises from 50 per cent. acetic acid in yellow, microscopic needles, melts at 205° , dissolves in alkalis forming a red solution, gives a violet coloration with concentrated sulphuric acid, and does not dye with mordants. By heating this substance with fuming hydrochloric acid at 130° , the methyl groups are eliminated, a dark green substance being formed which has not yet been obtained pure, but is probably either tetrahydroxyanhydrobisdiketohydrindene or an anhydride of this substance; it produces coloured lakes with mordants, those with the oxides of iron and aluminium being brown; in this respect, the compound resembles anthragallol, rufigallic acid, and the substance obtained by Kostanecki from diketohydrindene and protocatechuic aldehyde (Abstr., 1897, i, 425). G. T. M.

Metallic Derivatives of Dinitro- α -naphthol. By THOMAS H. NORTON and H. LOEWENSTEIN (*J. Amer. Chem. Soc.*, 1897, 19, 923—927).—A study of these compounds indicates that the metal is without influence on the tinctorial properties of the colouring matter.

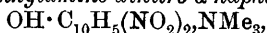
Lithium dinitro- α -naphthoxide, $C_{10}H_5(NO_2)_2 \cdot OLi$, produced by boiling an excess of dinitro- α -naphthol with an aqueous solution of lithium carbonate, separates as a crimson powder soluble in water, alcohol, and ether, but insoluble in carbon bisulphide and benzene.

Magnesium dinitro- α -naphthoxide, $[C_{10}H_5(NO_2)_2 \cdot O]_2Mg$, forms rosettes of red needles soluble in water, alcohol, and ether.

Zinc dinitro- α -naphthoxide, $[C_{10}H_5(NO_2)_2 \cdot O]_2Zn$, crystallises either in reddish-yellow needles, or in reddish, rhomboidal plates.

Copper dinitro- α -naphthoxide, $[C_{10}H_5(NO_2)_2 \cdot O]_2Cu$, is a dark brown powder, and the most insoluble salt of the series. All these salts are anhydrous, and explode when heated. G. T. M.

Amido-derivatives of Dinitro- α -naphthol, and its Chlorination. By THOMAS H. NORTON and IRWIN J. SMITH (*J. Amer. Chem. Soc.*, 1897, 19, 927—930).—*Trimethylamine-dinitro- α -naphthol*,



prepared by boiling dinitro- α -naphthol with an aqueous solution of trimethylamine, crystallises from alcohol in lustrous, red needles melting at 190° ; it is soluble in water, alcohol, and ether, and insoluble in carbon bisulphide and benzene.

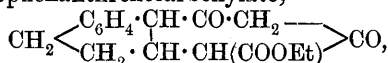
Aniline-dinitro- α -naphthol, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{NO}_2)_2 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_5$, prepared by heating together alcoholic solutions of dinitro- α -naphthol and aniline, crystallises in yellow needles melting at 129° ; it is soluble in hot water, alcohol, and ether, and sparingly so in carbon bisulphide and benzene.

Orthotoluidine-dinitro- α -naphthol, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{NO}_2)_2 \cdot \text{NH}_2 \cdot \text{C}_7\text{H}_7$, crystallises in yellow, silky needles melting at 132° ; it is more soluble than the preceding salt.

Dimethylaniline-dinitro- α -naphthol, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{NO}_2)_2 \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_5$, melts at 115° , and is soluble in water, alcohol, and ether, but insoluble in benzene.

Chlorination of dinitro- α -naphthol yields a dark yellow, viscous mass having no definite melting point; it is free from nitrogen and contains 13.7 per cent. of chlorine. G. T. M.

Synthesis of Phenanthrene and Hydrated Phenanthrene Derivatives from 1-Naphthoic Acid. By PAUL RABE (*Ber.*, 1898, 31, 1896—1902).—1-Naphthoic acid, obtained by heating 1-naphthonitrile with a mixture of sulphuric and acetic acids, was converted into Δ_1 -dihydro-1-naphthoic acid by reduction with sodium amalgam in warm alkaline solution, and from the acid, *ethylic* Δ_1 -dihydro-1-naphthoate, boiling at $305\text{--}306^\circ$ under 748 mm. pressure, was prepared; by heating this for 48 hours with alcoholic sodium ethoxide and ethylic acetoacetate, and acidifying the product with dilute sulphuric acid, an oil was obtained which consisted largely of ethylic diketo-octohydrophenanthrenecarboxylate,



for after hydrolysis with alcoholic potash, it yields an oily acid which, when heated on the water bath, loses carbonic anhydride and forms *diketo-octohydrophenanthrene*. This melts and decomposes at about 160° , and when distilled with zinc dust yields an oil which presumably is crude phenanthrene, for it can be oxidised to phenanthraquinone; the diketo-octohydrophenanthrene functions as a monobasic acid (the *barium* salt was analysed), so that one of the ketonic oxygens is capable of transformation into enolic hydroxyl; with diazobenzene chloride, it yields an orange *phenylhydrazone* which melts at 156° .

C. F. B.

Oil of Savin (*Oleum Sabinæ*). By EMIL FROMM (*Ber.*, 1898, 31, 2025—2031).—When fractionally distilled, oil of savin yields three fractions: the first comes over below 195° , and consists mainly of terpenes, which, on further fractionation, distil between 156° and 170° ; the second fraction distils between 195° and 235° , and consists mainly of ethereal salts; the third fraction passes over between 235° and 310° , and consists mainly of resins together with cadinene (Wallach, *Abstr.*, 1887, 596). The second fraction, when further fractionated, yields an oil passing over between 222° and 224° , and consisting of the acetate of an alcohol, $\text{C}_{10}\text{H}_{15} \cdot \text{OH}$, which the author terms *sabinol*. Schimmel and Co. have previously stated that the oil contains the acetate of an alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$. Sabinol is formed when the acetate (b. p. $222\text{--}224^\circ$) is hydrolysed with alcoholic potash, but is more readily obtained by

boiling the crude oil for half an hour with alcoholic potash, and then distilling in a current of steam; the oil which passes over is rectified, and by repeated fractionation the alcohol is obtained as a colourless oil, with a faint odour, and boiling at 208—209°. The yield is about 50 per cent. of the crude oil. Sabinol absorbs bromine, iodine, and hydrogen chloride, but crystalline products cannot be obtained. When treated with strong dehydrating agents, a small quantity of an oil, boiling at 175°, is obtained, together with a considerable quantity of resin.

When the alcohol is oxidised in the cold with a neutral saturated solution of potassium permanganate as long as the latter becomes decolorised, a quantitative yield of *α*-tanacetogendicarboxylic acid, $C_9H_{14}O_4$, is obtained. This acid, when heated to about 240°, loses carbonic anhydride and yields a monobasic acid, $C_8H_{14}O_2$; this can best be purified by dissolving it in sodium carbonate solution, and subsequently distilling, when it passes over at 229°. J. J. S.

Orientation in the Terpene Series: Conversion of Monocyclic Terpenes into the Corresponding Derivatives of Benzene. II. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1898, 31, 2067—2079. Compare this vol., i, 442).—When sylvestrene dihydrobromide is brominated and then reduced with zinc dust and hydrochloric acid, or sodium and alcohol, a hydrocarbon is obtained which, when freed from unsaturated compounds by the aid of potassium permanganate, is identical with metacymene.

The authors suggest the prefix *gem* (from "gem" twin) for compounds containing two alkyl groups attached to the same carbon atom; for example, unsymmetrical dimethylsuccinic acid is termed *gem*-dimethylsuccinic acid.

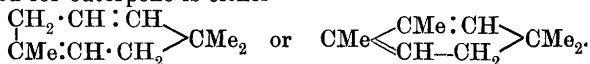
Eucarvone is obtained from carvone in the same manner as carone from dihydrocarvone, it is therefore probable that eucarvone differs from carone merely by a double linking, although the two compounds behave quite differently when oxidised. It has already been shown that carone, on oxidation, yields caronic acid or *gem*-dimethyltrimethylenedicarboxylic acid (Perkin and Thorpe, *Proc.*, 1898, 107), whereas dihydroeucarvone or methyl-*gem*-dimethylcycloheptenone, when oxidised with a saturated solution of potassium permanganate, yields *gem*-dimethylsuccinic acid. It then follows that the *gem*-dimethyl group which is present in eucarvone is also present in dihydroeucarvone; the presence of the double bond, however, prevents the determination of the constitution of the other part of the molecule. The ketone, when reduced with sodium and alcohol, yields dihydroeucarvol. Dihydroeucarvonoxime hydriodide, when reduced with sodium and alcohol, yields dihydroeucarvylamine, but with zinc dust and an alcoholic solution of hydrogen chloride at 0°, yields *tetrahydroeucarvone*, $C_{10}H_{18}O$, and this, when freed from unsaturated compounds by treatment with potassium permanganate, distils at 108—115° under a pressure of 20 mm. Its *oxime* does not crystallise, but its *semicarbazone*, $C_{11}H_{21}N_3O$, crystallises from ethylic acetate in fine needles melting at 191°, and is sparingly soluble in both ether and ethylic acetate. Tetrahydroeucarvone is not acted on by amylic nitrite and

hydrochloric acid, but the dihydroketone readily yields a bisnitroso-compound.

The theoretical quantity of cold 4 per cent. potassium permanganate oxidises tetrahydroeucarvone to the *ketonic acid*, which is best purified by conversion into its *semicarbazone*, $C_{11}H_{21}N_3O_2$, in the process of oxidation, about two-thirds of the ketone remains unaltered. The semicarbazone, which is sparingly soluble in the usual solvents with the exception of chloroform and acetic acid, crystallises from its warm ethylic acetate solution in long needles melting at 191° . The *oxime*, $C_{10}H_{19}NO_3$, of the ketonic acid crystallises in transparent, glistening prisms melting at $101-102^\circ$. The ketonic acid regenerated from the semicarbazone could not be obtained in a crystalline form; that it is a methyl ketone was proved by its reaction with sodium bromide. The chief product of the oxidation of the ketone with cold permanganate is *gem*-dimethyladipic acid, $C_8H_{14}O_4$, crystallising from an ethereal light petroleum solution in prisms melting at $87-88^\circ$ (compare Tiemann, this vol., i, 374). When the ketone (5 grams) is heated on the water bath for 18 hours with permanganate (66 grams) and water (1.5 litres), a mixture of acetic, oxalic, dimethylmalonic, and *gem*-dimethylsuccinic acids is obtained.

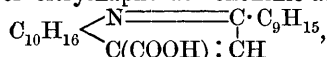
A hydrocarbon *euterpe* is obtained when dihydroeucarvol (100 grams) is treated with phosphorus pentachloride (200 grams), and the chloro-derivative thus formed, after removal of the phosphorus oxychloride, is boiled with quinoline for half an hour. This terpene boils at $161-165^\circ$, and when oxidised with permanganate yields acetic, oxalic, and *gem*-dimethylsuccinic acids.

Euterpe yields a dihydrobromide, which, when treated with bromine in the presence of iodine and then reduced in the manner previously described (this vol., i, 442), yields a hydrocarbon, 1:2:4-dimethylethylbenzene, boiling at $185-191^\circ$. The constitution suggested for euterpe is either



J. J. S.

Citral. By OSCAR DOEBNER (*Ber.*, 1898, 31, 1888-1896).—The amount of citral present in various ethereal oils was determined by finding the amount of citrylnaphthacinchoninic acid,



they would yield when heated with pyruvic acid and β -naphthylamine in alcoholic solution (*Abstr.*, 1894, i, 261, 532). Of those oils in which citral is known to occur, none contain more than an inconsiderable quantity, except lemon oil, from *Citrus limonum*, which contains 7-8, and lemon-grass oil, from *Andropogon citratus*, which contains 80-82 per cent.

The ketone obtained by the action of bleaching powder on lemon-grass oil and acetone in alcoholic solution, and "inverting" the pseudoketone thus obtained, by boiling it with a solution of sodium hydrogen sulphate (Fritsche and Co., English Patent, No. 26350), is shown conclusively to be nothing but the α -ionone of Tiemann and Krüger (*Abstr.*, 1893,

i, 82; this vol., i, 376), mixed with a certain quantity of optically active terpenes and other substances not of an aldehydic nature (originally present in the lemon-grass oil), which confer optical activity on the mixture. As regards the reaction, the bleaching-powder is all destroyed in a few minutes, chloroform being formed; at this stage, the lemon-grass oil is still unchanged, however, and it is only by the subsequent action of the calcium hydroxide contained in the bleaching powder that it is converted into the pseudoketone.

C. F. B.

Oil of Violets from Oil of Lemon-grass. By J. ZIEGLER (*J. pr. Chem.*, 1898, [ii], 57, 493—495).—The author calls attention to the fact (English Patent, No. 26350/96, &c.) that he has prepared a ketone similar to, but different from, pseudoionone by heating lemon-grass oil, or, better, those fractions of it which contain but little citral, with acetone, bleaching powder, dilute alcohol, and a little cobalt nitrate. By boiling this product for several days with a solution of sodium hydrogen sulphite, it is possible to convert it into an isomeride, which resembles ionone, but is not identical with that substance; it has been put on the market as “artificial oil of violets.” C. F. B.

[NOTE BY ABTRACTOR.—Doebner (preceding abstract) appears to have shown that the two substances in question are nothing else than impure pseudoionone and ionone. The discrepancy awaits explanation.]

Ionone from Lemon-grass Oil. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1898, 31, 2313—2329).—It is shown in this paper that citral is the only considerable aldehydic constituent of lemon-grass oil. The author replies in detail to the criticisms of Ziegler (preceding abstract) on his previous communications (this vol., i, 374).

M. O. F.

Amidoborneol. [By PAUL DUDEN and ALFRED E. MACINTYRE (*Ber.*, 1898, 31, 1902—1904).—When amidocamphor (Claisen and Manasse, *Abstr.*, 1893, i, 479) is reduced in boiling alcoholic solution with excess of sodium, it yields *amidoborneol*, $C_{10}H_{19}NO$, which melts at 187° , boils at 264° under a pressure of 751 mm., and shows a tendency to sublime; it also crystallises with water, and then melts at about 90° . Its *hydrochloride* decomposes at 285° , the yellowish *platinochloride* at 272° , the *aurochloride* at 190° ; the yellow *picrolonate* (*Abstr.*, 1897, i, 314) melts and decomposes at 272° ; the *carbamide* melts at 177° , the *acetyl* derivative at 170° ; the *methiodide* decomposes above 270° .

C. F. B.

A Crystalline Heptacetin derived from Ouabin. By ALBERT ARNAUD (*Compt. rend.*, 1898, 126, 1654—1656).—When finely-powdered anhydrous ouabin, $C_{30}H_{46}O_{12}$, is gently warmed with acetic anhydride and a little zinc chloride, it loses a molecule of water and is converted into a crystalline *heptacetate*, which analysis shows to have the composition $C_{30}H_{37}Ac_7O_{11}$. At the same time, a large proportion of an amorphous acetyl compound is produced, which is very soluble in alcohol and other solvents, and appears to be derived from a substance resulting from a more advanced dehydration of ouabin. The crystal-

line heptacetate is almost insoluble in water and in ether, slightly soluble in cold alcohol and acetic acid, readily in ethylic acetate, acetone, and hot alcohol. It crystallises in thin, rhombic, anhydrous plates which melt and decompose rapidly at about 310° . The alcoholic solution is laevorotatory, $[\alpha]_D = -68.5^{\circ}$ at 85° . The heptacetate is converted by hydrolysis with alkalis into an amorphous *acid* substance which resembles ouabaic acid in its properties, but differs from it in possessing a much lower rotatory power. This acid, when boiled with dilute mineral acids, yields an insoluble resin and a considerable quantity of rhamnose. From these results, it follows that the molecule of ouabin contains nine hydroxyl groups; four of these belong to the rhamnose molecule, whilst the other five, connected in an as yet unknown manner, lose a molecule of water previous to the formation of the heptacetate.

N. L.

Jalapinolic Acid. By NICOLAI KROMER (*J. pr. Chem.*, 1898, [ii], 57, 448—466).—Jalapic acid was prepared from false jalap resin, and boiled with dilute hydrochloric acid; the jalapinolic acid, $C_{16}H_{32}O_3$, thus obtained was purified by converting it into its methylic or ethylic salt and recrystallising these first from light petroleum and then from ether; they melt at 50 — 51° and 47 — 48° respectively, and solidify at 43 — 42° and 41 — 40° ; the purified acid melts at 67 — 68° , and is optically inactive; the silver salt was analysed.

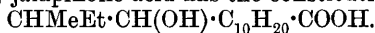
When the ethylic salt is heated with acetic anhydride and sodium acetate, a *monacetyl* derivative is formed, which boils at 224 — 225° under 50 mm. pressure.

Jalapinolic acid forms no additive product with bromine, but yields a liquid substitution product, which, however, was found not to be homogeneous.

When the methylic salt is mixed with phosphorus iodide and the mixture is moistened with hydriodic acid and allowed to remain for 24 hours, the product being finally reduced with zinc and hydrochloric acid in boiling alcoholic solution, an *acid*, $C_{16}H_{32}O_2$, is obtained, melting at 65 — 66° , solidifying at 63 — 62° , and having the character of a saturated compound; it is not identical with any of the acids of this composition already known.

When the acid (1 mol.) is oxidised with potassium permanganate (4 atoms) in alkaline solution at 50° , methylethylacetic acid, sebacic acid, and an acid melting at 89 — 91° , and possibly isomeric with sebacic acid, are formed.

Probably, then, jalapinolic acid has the constitution



C. F. B.

Lupulinic Acid. By GEORG BARTH and CARL J. LINTNER (*Ber.*, 1898, 31, 2022—2025).—Hop resin yields two crystalline substances having a bitter taste and a slightly acidic nature; they are termed α - and β -hop-bitter acids. The latter is identical with Bungener's lupulinic acid, obtained by extracting lupulin with light petroleum. To remove all traces of waxy and resinous substances, the acid is repeatedly crystallised from light petroleum and finally from 90 per cent. methylic alcohol; from the latter solvent, it crystallises in

glistening prisms which melt at 92° and become resinous on exposure to the air. The mean of ten analyses gave $C = 75.0$; $H = 9.17$ per cent., which correspond with the formula $C_{25}H_{36}O_4$; Bungener supposed the acid to have the formula $C_{25}H_{35}O_4$, and in Beilstein's handbook the double formula, $C_{50}H_{70}O_8$, is given. Determinations of the molecular weight by the depression of the freezing point, the rise in boiling point, and titration with standard alkali, all give numbers closely approximating to the simple formula $C_{25}H_{36}O_4$.

The acid reduces ammoniacal silver solutions, and when oxidised with permanganate in alcoholic solution valeric acid is formed; it does not give crystalline derivatives with phenylhydrazine, semicarbazide, or hydroxylamine. The authors believe that both the above α - and β -hop-bitter acids are derived from the terpenes, and stand in close relationship to the other ingredients of the oil of hops.

G. T. M.

Yohimbine. By OBERWARTH (*Virchow's Archiv*, 1898, 153, 292—305).—An extract of the acid of the rind of the yohimbehe has been recommended as an aphrodisiac. Two substances named yohimbine and yohimbenine have been separated from it. The physiological action of the latter is weaker than, but is otherwise similar to, that of the former. Yohimbine is an alkaloid melting at 234° ; its hydrochloride melts at 287° . It produces paralysis of the nervous system after preliminary convulsions. It weakens, then stops the heart; blood pressure falls. Death is produced by paralysis of the respiratory apparatus. (Compare this vol., i, 455.)

W. D. H.

Lichens and their Characteristic Constituents. By OSWALD HESSE (*J. pr. Chem.*, 1898, [ii], 57, 409—447. Compare this vol., i, 531).—*Parmelia perlata* (L) Ach. = *Imbricaria perlata* Körber.—A specimen from the neighbourhood of Stuttgart contained atranorin only. Another, from American cinchona bark, contained usnic acid and atranorin, and a little vulpic acid; the atranorin was erroneously described as a new substance, parmelin, in an earlier paper (Abstr., 1895, i, 299). A third specimen, from Java cinchona bark, contained atranorin and lecanoric acid; the varieties with grey thallus contained very little of this acid, those with a greenish-grey thallus, which become coloured by bleaching powder solution, contained more. In one sample, the atranorin was found to be accompanied by a new substance, *perlatin*, $C_{19}H_{14}O_5(OMe)_2$, which can be dissolved out with alcohol. This crystallises in pale yellow prisms; hydriodic acid eliminates the methyl from it, forming crystalline *norperlatin*, which begins to sublime at 250° and melts at 274° and has not the character of an acid.

P. physodes (L) Ach. = *P. ceratophylla* (Wallroth) = *Imbricaria physodes* Körber, from the neighbourhood of Stuttgart.—From the ethereal extract, atranorin and capraric acid first crystallised, extraction with potassium hydrogen carbonate solution dissolving out the latter. By extracting the ethereal mother liquor with potassium hydrogen carbonate solution, capraric acid (see under *P. caperata*) and physodic acid were obtained, and were separated by treatment with lime- or strontia-water, which yield insoluble salts with capraric acid. Final

evaporation of the ethereal solution yields an amorphous substance, *physol*, $C_{20}H_{24}O_5$, which melts at about 145° , contains no methoxyl, has the characters of an alcohol, and, in alcoholic solution, oxidises spontaneously to physodic acid. *Physodic acid*, probably $C_{19}H_{19}O_2(OH)_2 \cdot COOH$, which melts and decomposes at $190-192^\circ$, contains no methoxyl; it forms a *diacetyl* derivative melting at 158° , and a series of ill-defined salts. When boiled with baryta solution, it loses carbonic anhydride, and yields a product obtained only as a reddish syrup, whilst prolonged boiling with alcohol, ether, or other organic solvents converts the acid into an amorphous isomeride. The ceratophyllin formerly found in this acid was methylic betorcinolcarboxylate, and had been formed by the action of the hot sodium carbonate solution on the atranorin. The substance described as physodin was probably slightly impure capraric acid.

P. caperata (L.) Ach. = *Imbricaria caperata*, Körber, from Stuttgart and Heidelberg.—From the ethereal extract, capraric acid separated first, mixed with usnic acid, which could be dissolved out with benzene; caperatic acid remained in solution. In specimens that had grown on oak trees, caperin and caperidin separated out in addition; these remain when the whole mixture is extracted with potassium carbonate solution, and can be crystallised from alcohol or benzene, from which the caparidin separates first. *Capraric acid*, $C_{22}H_{18}O_8(COOH)_2$, crystallises in white needles, which begin to decompose at about 240° ; the amorphous *barium* salt was analysed. When treated with boiling acetic anhydride, the acid yields an amorphous *anhydride*, $C_{24}H_{18}O_{11}$; and if boiled with alcoholic potash, a substance is formed which loses carbonic anhydride when heated with hydrochloric acid, yielding *capraric acid*, presumably $C_{23}H_{20}O_{10}$, and this, when dried at 100° , loses water and forms *capranide*, $C_{46}H_{38}O_{19}$. *Caperatic acid*, $COOMe \cdot C_{18}H_{33}O_2(COOH)_2$, is crystalline, and melts at 132° ; the amorphous *barium* and *silver* salts were analysed; when heated with acetic anhydride, it forms an anhydride, *caperatide*, which is crystalline and melts at 47° ; when heated with hydriodic acid, it loses methoxyl, and forms tribasic *norcaperatic acid*, which melts at 138° , crystallises with $2H_2O$, and perhaps contains two hydroxyl groups; the amorphous *barium* salt of this acid was analysed. *Caperin*, $C_{36}H_{60}O_9$, is a crystalline substance which melts at 243° , and has a very inert character; neither strong sulphuric, nitric, nor hydriodic acid reacts with it. When heated for 24 hours with absolute alcohol at 150° , it forms *dicaperin hydrate*, $C_{72}H_{120}O_6 + H_2O$, which melts at $227-228^\circ$, and when a solution of caperin in benzene is evaporated rapidly, *dicaperin*, $C_{72}H_{120}O_6$, melting at $248-250^\circ$, is deposited in slender needles. Molecular weight determinations in chloroform solution, by the boiling point method, show that this substance dissolves at first with the double molecular weight, but after a time suddenly dissociates into caperin; any further quantity of dicaperin now added to the solution is at once dissociated. *Caperidin*, $C_{24}H_{40}O_2$, is crystalline and melts at 262° ; it is also a chemically inert substance.

P. conspersa (Ehrh.) Ach. = *Imbricaria conspersa* Körber.—Usnic acid, and another acid not identified and possibly identical with Zopf's salazinic acid (this vol., i, 90).

Physcia stellaris (L.) f. *adscendens* (Fr.) Th. Fr.—Atranorin only (compare Zopf, *P. tenella*, Abstr., 1896, i, 103).

Xanthoria parietina (L.) Th. Fr. = *Parmelia parietina* (Ach.), *Physcia parietina* (Nyl.).—The physciol and physcianin previously found in this lichen (Abstr., 1895, i, 300) were not present originally, but were formed by the action of the hot sodium carbonate solution on the atranorin. Atranorin predominates in pale yellow to green specimens that have grown in the shade and in moist places; physcion in bright yellow specimens. Heating with hydriodic acid, or with a mixture of hydrochloric and acetic acids, eliminates methyl from physcion, forming protophyscion. The further action of hydriodic acid leads to the formation of protophyscihydrone, $C_{15}H_{12}O_4$, which is also the product of the action of zinc powder on protophyscion. Prolonged heating with methyl alcoholic potash and methylic iodide converts physcion into two isomeric *methylphyscions*, $C_{15}H_8Me_2O_5$; the α -compound is yellow and melts at 205° , whilst the β -compound is red, melts at 178° , and is more soluble than the other in acetic acid.

X. lichnea (Ach.) Th. Fr.—Physcion only.

X. Candelaria (Ach.) from Berchtesgaden, Brand in the Vorarlberg, and Stuttgart.—Physcion only.

Candelaria concolor (Dicks.) Th. Fr., from Stuttgart, &c.—Dipulvic acid, $C_{36}H_{22}O_9$; this forms red needles and melts at 211° ; heated with acetic anhydride, it yields yellow pulvic anhydride, $C_{18}H_{10}O_4$, melting at 214° , and after crystallisation from benzene, at 220° . The calycin found by Zopf (Abstr., 1895, i, 298) was dipulvic acid; the ethylpulvic acid (this vol., i, 90) was formed by the action on the dipulvic acid of small quantities of alcohol present in the ether used.

Sticta pulmonaria (L.) Schaerer.—Protocetraric acid.

Nephromium lævigatum (Ach.) Nylander, and *N. tomentosum* (Hoffm.) Nylander, from Nyborg in Finland.—The ether extract leaves a residue from which light petroleum removes a wax-like substance; when what remains is crystallised from benzene, usnic acid crystallises first, and then a new substance, *nephtrin*, which melts at 168° and appears to be a diterpene hydrate, $C_{20}H_{32} + H_2O$.

N. lusitanicum (Schaerer) from the island of Miquelon and from Brittany.—The ether extract gave a residue which was recrystallised from acetic acid; nephtrin separated first, and then a new substance, *nephromin*, $C_{16}H_{12}O_6$ ($= C_{15}N_9O_5 \cdot OMe?$), mixed with some wax, which was removed with light petroleum. *Nephromin*, which is ochre-coloured, melts and decomposes at about 196° . With alkalis, it forms red solutions, in which it ultimately becomes transformed into an amorphous substance; it is closely related to physcion.

Gasparrinia medians (Nylander) = *Physcia medians* (Nyl.).—Calycin and rhizocarpic acid; no ethylpulvic acid (Zopf, Abstr., 1895, i, 298).

G. elegans (Lk.) Tornab. = *Amphiloma elegans* Körber = *Physcia elegans* Nylander, from the neighbourhood of Stuttgart and of Salzburg, and from the Vorarlberg.—Physcion only.

G. murorum (Hoffm.) Tornab. = *Amphiloma murorum* Körber, from Stuttgart.—Physcion only.

G. decipiens Arnold from Stuttgart.—Physcion only.

C. F. B.

The Chemistry of Chlorophyll. By G. BODE (*J. pr. Chem.*, 1898, [ii], 57, 488—493). A reply to Marchlewski (this vol., i, 536).

Colouring Matter of Cochineal. By CARL LIEBERMANN (*Ber.*, 1898, 31, 2079—2084).—Carminic acid is probably an indene derivative having the composition $C_{22}H_{22}O_{13}$ (compare Abstr., 1897, i, 539 and 540); the author is engaged in the study of its derivatives, and of its products of decomposition. The acid, which is itself readily soluble in water, readily passes into insoluble colouring matters, the change being accompanied by an elimination of water and an increase in molecular complexity; this change is characteristic of the keto-indene series (Abstr., 1887, 587, and 1889, 1067). With a view to studying the properties of similarly constituted compounds, the author condenses dibromindone with diethylic malonate in the presence of sodium ethoxide. The condensation product which results from the combination of dibromindone and diethylic malonate, in molecular proportion, is provisionally termed *diethylic bromindone malonate*; it crystallises from dilute alcohol in yellow leaflets and melts at 129—130°. Purple colorations are developed with alcoholic and aqueous alkalis, but it does not dye wool either with or without mordants. Its constitution may be either $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CBr \end{smallmatrix} > C \cdot CH(COOEt)_2$ or $CO \begin{smallmatrix} \diagup CBr \\ \diagdown C_6H_4 \end{smallmatrix} > C \cdot CH(COOEt)_2$.

Ethylic bromindoneacetoacetate, $C_{15}H_{13}BrO_4$, is similarly prepared, melts at 80—82°, and gives similar colorations with alkalis.

Neither Roser's hydroxybromindone, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown C(OH) \end{smallmatrix} > CBr$, nor α -, nor β -bromocarmin yield colouring matters with diethylic malonate.

G. T. M.

Ethereal Indoxylates. By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Annalen*, 1898, 301, 349—352. Compare Blank, this vol., i, 589).—Ethereal salts of phenylglycine-carboxylic acid are converted into ethereal indoxylates, $C_6H_4 \begin{smallmatrix} \diagup NH \\ \diagdown C(OH) \end{smallmatrix} > C \cdot COOR$, when gently heated with sodium ethoxide.

Dimethylic phenylglycine-orthocarboxylate crystallises in elongated leaflets, and melts at 97°; the *diethylic* salt melts at 75°. On heating these compounds, dissolved in benzene or ether, with sodium ethoxide, the corresponding salts of indoxylic acid are formed.

Methylic indoxylate melts at 155—157°.

M. O. F.

The Base prepared by E. Fischer from Methylketol and Methylic Iodide. By KARL BRUNNER (*Ber.*, 1898, 31, 1943—1949. Compare this vol., i, 384; also Plancher, this vol., i, 536).—Just as Fischer's base is obtainable from methylisopropylmethylphenylhydrazone, the hydriodide of 1'-phenyl-3':3'-dimethyl-2'-methyleineindoline, $C_6H_4 \begin{smallmatrix} \diagup CMe_2 \\ \diagdown NPh \end{smallmatrix} > C \cdot CH_2$, is produced by the action of alcoholic hydrogen iodide on methylisopropylidiphenylhydrazone.

The *hydriodide*, $C_{17}H_{17}N \cdot HI$, which crystallises from boiling 90 per cent. alcohol in pale yellow prisms, melts at 192°, and decomposes at 195°, evolving gas. The salt dissolves with difficulty in cold water,

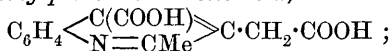
but is freely soluble in hot water, forming a turbid solution. 1'-Phenyl-3':3'-dimethyl-2'-methyleineindoline boils at 183—185° under a pressure of 32 mm., and does not solidify at -10°. It is a colourless oil having a spice-like odour, and resembles Fischer's base, not only in the property of becoming magenta red when exposed to air, but also in the formation of a yellow, oily precipitate gradually becoming crystalline, which is produced when ferric chloride is added to the solution in hydrochloric acid. The *picrate* forms yellow leaflets, and melts at 111°; the *sulphate* crystallises in needles, and melts at 206°, above which temperature it decomposes and evolves gas.

M. O. F.

Condensations of Isatic Acid with Formation of Derivatives of Cinchonic Acid. By C. ENGELHARD (*J. pr. Chem.*, 1898, [ii], 57, 467—484. Compare Pfitzinger, this vol., i, 207).—Isatic acid, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{COOH}$, prepared by boiling isatin with 30 per cent. potash, condenses with dibenzyl ketone when the latter and some alcohol are added to the alkaline solution of isatic acid, and the whole is boiled for several hours. The product is 3'-phenyl-2'-benzylquinoline-4'-carboxylic acid [quinoline-4'-carboxylic acid = cinchonic acid]; it melts at 293—295°, and has feeble basic, but more pronounced acid properties; its *silver* salt was analysed; when heated alone or with soda lime, it yields 3'-phenyl-2'-benzylquinoline as an oil; its orange-yellow *platinochloride* melts at 208°, and crystallises with $2\text{H}_2\text{O}$.

With ethylic benzoacetate, isatic acid condenses, in alkaline solution at the ordinary temperature, to 2'-phenylquinoline-3':4'-dicarboxylic acid, which melts at 193—194°, and crystallises with $2\text{H}_2\text{O}$; the *silver* salt was analysed.

With levulinic acid, isatic acid condenses in boiling, alkaline solution to 4'-carboxy-2'-methylquinoline-3'-acetic acid,



this begins to decompose at about 280°; the *silver* salt was analysed. When distilled with soda-lime, the acid yields 2':3'-dimethylquinoline (Rhode, *Abstr.*, 1887, 974; 1889, 523). As the CH_3 -group in levulinic acid standing at the end of the chain has not reacted, probably the same would hold for acetoacetic acid, and if so, the compound prepared by Pfitzinger from this acid and isatic acid would be 2'-methylquinoline-3':4'-dicarboxylic acid, and not the 2':4'-dicarboxylic acid.

Paramethylisatic acid reacts with ethylic acetoacetate in cold alkaline solution, and the 3':2'-dimethyl-3':4'-dicarboxylic acid thus formed melts at 233—234°; its *silver* salt, with $2\text{H}_2\text{O}$, is very hygroscopic.

Isatic acid in cold alkaline solution condenses with ethylic acetone-dicarboxylate, forming 3'(or 4')-carboxy-2'-methylquinoline-2'-acetic acid, carbonic anhydride being liberated. The acid, which is pale yellow, melts at 228—229° and crystallises with $1\text{H}_2\text{O}$; the *silver* salt was analysed.

Attempts to prepare quinoline-2':3':4'-tricarboxylic acid, by condensing isatic acid in alkaline solution with ethylic oxalacetate, and

by oxidising Pfitzinger's methylquinolinedicarboxylic acid with chromic and sulphuric acids, were unsuccessful. In the first case, the oxalacetate was decomposed and the isatic acid remained unchanged; in the second, most of the dicarboxylic acid was completely oxidised and the rest remained unchanged.

C. F. B.

Synthesis of *d*- and *l*-Ethylpiperidine. By ADOLF GÜNTHER (*Ber.*, 1898, 31, 2134—2142).—*Ethyl* γ -phenoxypropylethylmalonate, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CEt}(\text{COOEt})_2$, prepared by acting on ethyl γ -phenoxypropylmalonate with sodium and ethyl iodide, forms a colourless syrup boiling at $227\text{--}230^\circ$ under a pressure of $22\text{--}23\text{ mm.}$ γ -Phenoxypropylethylmalonic acid, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{CEt}(\text{COOH})_2$, is formed when the ethyl salt is treated with potash; it dissolves readily in the ordinary solvents with the exception of water, and crystallises from ether in fine, prismatic needles which melt at $89\text{--}90^\circ$, and rapidly loses carbonic anhydride at $140\text{--}200^\circ$. A solution of the ammonium salt gives a white precipitate with calcium chloride, and a bright green, indistinctly crystalline precipitate with copper sulphate; the copper salt melts and decomposes at $231\text{--}233^\circ$, whilst the silver salt forms a white, amorphous powder.

δ -Phenoxy- α -ethylvaleric acid, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{CHEt}\cdot\text{COOH}$, formed from phenoxypropylethylmalonic acid when it is heated at $140\text{--}200^\circ$, boils at $322\text{--}323^\circ$ and forms stellate groups of needles melting at $60\text{--}63^\circ$; it dissolves readily in alcohol and ether, and may be crystallised from light petroleum. When heated with lead thiocyanate at $200\text{--}220^\circ$, it yields δ -phenoxy- α -ethylvaleronitrile, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{CHEt}\cdot\text{CN}$, which boils at $315\text{--}317^\circ$.

ϵ -Phenoxy- β -ethylamylamine, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{NH}_2$, obtained by reducing phenoxyethylvaleronitrile with sodium and alcohol, has the odour characteristic of fatty amines, and yields a semi-crystalline hydrochloride, and a picrate, $\text{C}_{19}\text{H}_{24}\text{O}_8\text{N}_4$; this crystallises in fine, lemon-yellow needles, and melts at $104\text{--}106^\circ$ to a reddish-yellow, transparent liquid which, on cooling, sets to a mass of leaflets.

ϵ -Chlor- β -ethylamylamine, $\text{C}_3\text{H}_6\text{Cl}\cdot\text{CHEt}\cdot\text{NH}_2$, is formed when the hydrochloride of phenoxyethylamylamine is heated with hydrochloric acid at 100° during 20 hours. The picrate, $\text{C}_7\text{H}_{16}\text{ClN}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises in fine, yellow needles melting at 145° ; the platinochloride, $(\text{C}_7\text{H}_{17}\text{NCl})_2\cdot\text{PtCl}_4$, forms microscopic, yellow needles which blacken at 225° , and decompose at $242\text{--}244^\circ$.

When chlorethylamylamine is heated with excess of potash in closed vessels on the water bath, it loses hydrogen chloride and yields β -ethylpiperidine; this is isolated by steam distillation, neutralisation of the distillate with hydrogen chloride, and evaporation to dryness. The hydrochloride thus obtained, as well as the picrate and platinochloride, have the same melting points and properties as those formed from Stoehr's base (*Abstr.*, 1892, 628). The free base is a transparent, limpid liquid of coniine-like odour, boiling at $154\text{--}155^\circ$; it fumes in the air and has a sp. gr. = 0.871 at $16^\circ/4^\circ$. Its physiological properties resemble those of β -propylpiperidine (*Abstr.*, 1897, i, 437), but are much less marked.

The resolution of β -ethylpiperidine into its optical antipodes was

accomplished by Marckwald's method (Abstr., 1896, 42). 1- β -*Ethylpiperidine d-hydrogen tartrate* crystallises in fine tablets or needles, and melts to a brown liquid at 169—170°. 1- β -*Ethylpiperidine* boils at 155° and has a rotation $[\alpha]_D = -4.51^\circ$ at 15°; its *hydrochloride* forms silky needles and melt at 142°. d- β -*Ethylpiperidine l-hydrogen tartrate* forms plates which turn to feather-like crystals, and melt at 174° to a brown liquid. d- β -*Ethylpiperidine* is dextrorotatory, and affords a *hydrochloride* which melts at the same temperature as that made from the lævo-base.

A. L.

Some Bases Derived from Piperidine. By GUSTAVE ANDRÉ (*Compt. rend.*, 1898, 126, 1797—1799).—Ethylenedipiperidine, $C_2H_4(C_5NH_{10})_2$, and also the dihydrobromide of this base, have been already described by Brühl. The *dihydrochloride*, which is readily formed by the action of ethylenic chloride on piperidine, crystallises in fine needles, and when boiled with aqueous potash, is converted into ethylenedipiperidine; the latter is also easily prepared by boiling a mixture of ethylenic bromide (1 mol.) and piperidine (2 mols.) with excess of aqueous potash in a reflux apparatus. Ethylenedipiperidine was thus obtained as a colourless oil having a faint odour of piperidine; it boils at 261° under a pressure of 760 mm., and has a sp. gr. = 0.9364 at 0°. Brühl describes this base as becoming solid at 4°, but the author was unable to solidify it even at -23°. Ethylenedipiperidine readily combines with water to form a *hydrate* of the composition $C_2H_4(C_5NH_{10})_2 + 3H_2O$, which melts and dissociates on heating. Attempts were made to prepare a base isomeric with ethylenedipiperidine by the action of ethylenic chloride or bromide on piperidine. The products obtained appear, however, to be mixtures of various compounds, and such a base, if it exists at all, is probably very unstable.

Methylethylenedipiperidine, $C_5NH_{10} \cdot CHMe \cdot CH_2 \cdot C_5NH_{10}$, obtained by the action of aqueous potash on a mixture of propylenic bromide with piperidine, is an oily liquid boiling at 268—269° under a pressure of 745 mm., and having a sp. gr. = 0.9225 at 16°; it does not solidify when cooled to the temperature of boiling methylic chloride. It is nearly insoluble in water, but forms with it a crystalline *hydrate* which is only stable at a low temperature.

Trimethylenedipiperidine, $CH_2(CH_2 \cdot C_5NH_{10})_2$, which has been previously prepared by Töhl, was obtained by the action of trimethylenic bromide on piperidine in presence of potash, as a liquid boiling at 278—279° under a pressure of 752 mm., and having a sp. gr. = 0.9183 at 16°; it does not solidify at -23°. When shaken with a little water and cooled, it forms a crystalline *hydrate* of the composition $C_3H_6(C_5NH_{10})_2 + 8H_2O$, which dissociates at the ordinary temperature.

Trimethylenoldipiperidine, $OH \cdot CH(CH_2 \cdot C_5NH_{10})_2$, is obtained when α -dibromhydrin is warmed with piperidine in presence of aqueous potash; it boils at 171—172° under a pressure of 15 mm., and has a sp. gr. = 0.9812 at 15°.

Methylolethylenedipiperidine, $C_5NH_{10} \cdot CH_2 \cdot CH(CH_2 \cdot OH) \cdot C_5NH_{10}$, from β -dibromhydrin and piperidine, boils at 178—180° under a pressure of 23 mm., and has a sp. gr. = 0.9877 at 15°. It resembles

the preceding compound in forming a well-crystallised platinochloride, and in not yielding a hydrate by prolonged agitation and cooling with water.

N. L.

Syntheses in the Piperidine Series. By FELIX B. AHRENS (*Ber.*, 1898, 31, 2272—2276. Compare Abstr., 1897, i, 368).—The base, $C_{10}H_{18}N_2$, obtained by the electrolysis of nitrosopiperidine yields a *dithiocarbanilide*, $C_{10}H_{16}N_2(CS \cdot NPh)_2$, melting at 183° , and an oily *monobenzoyl* derivative, which, on further treatment with benzoic or acetic anhydride, gives rise to tarry products. Two isomeric bases, $C_8H_{11}N$, differing markedly from piperidine, are produced from the above diamine, on reduction with tin and hydrochloric acid; the α -base, its salts, and its benzene sulphonamide are oily, whilst the β -base and its derivatives are solids, the *benzenesulphonamide* melts at 160° .

Amido-acids are also produced by the electrolytic oxidation of nitrosopiperidine in sulphuric acid; an acid which was not definitely characterised has been previously mentioned, and a second acid has now been obtained by treating the product of electrolysis with barium hydroxide and carbonic anhydride successively, evaporating to dryness the filtrate from the barium carbonate, and liberating the acid with sulphuric acid. Neither the acid nor its metallic salts could be obtained crystalline, but a well-defined *platinochloride* crystallising from water in yellow leaflets, and melting at 170° , indicates that the acid is an amidovaleric acid.

Two volatile bases are also produced in this reaction, and are distilled off from the above product of electrolysis after it has been rendered alkaline with barium hydroxide; they are separated by means of their aurochlorides. Both of these salts have the composition $(C_5H_{11}N) \cdot HAuCl_4$; the less soluble melts at 206° , and the free base is found to be identical with piperidine; the more soluble aurochloride melts at 213° .

G. T. M.

Electrolysis of Nitroso- α -pipecoline and Nitrosotetrahydroquinoline. By RICHARD WIDERA (*Ber.*, 1898, 31, 2276—2278. Compare previous abstract).—A solution of nitroso- α -pipecoline in 30 per cent. sulphuric acid, electrolysed at the anode of an electrolytic cell, yields an *amidocaproic* acid of unknown constitution; its hydrochloride melts at 196° , and its platinochloride at 204° .

When the product of electrolysis is rendered alkaline and steam distilled, the distillate contains ammonia, α -pipecoline, and an oily diamine, which yields a *monothiocarbanilide*, $C_{12}H_{23}N_2 \cdot CSNPh$, melting at 116° .

The electrolysis of nitrosotetrahydroquinoline at the anode yielded only tetrahydroquinoline.

G. T. M.

Syntheses in the Piperidine Series. III. By FELIX B. AHRENS (*Ber.*, 1898, 31, 2278—2280).—It is well-known that pyridine bases are converted into derivatives of dipyridyl under the influence of sodium. The author has found that when the metal is suspended in a solution of nitrosopiperidine in dry ether, γ -dipiperidyl is produced, along with a small proportion of piperylhydrazine. Benzoylpiperidine yields piperidine, benzoic acid, and two compounds having the em-

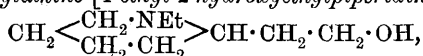
pirical formulæ of benzoyldipiperidyl and dibenzoyldipiperidyl respectively.
M. O. F.

aaa'a'-Tetramethyldipyriddy. By FRANZ HUTH (*Ber.*, 1898, 31, 2280—2282).—2:6-Dimethylpyridine resists the action of metallic sodium at the temperature of boiling water, but when heated with it in sealed tubes at 180—200° during 8—10 hours, yields *aaa'a'-tetramethyldipyriddy*, $C_{14}H_{16}N_2$, which crystallises from boiling water in long, white needles, and melts at 148—149°. The *platinochloride* crystallises in long, reddish-yellow needles, and does not melt below 280°; the *picrate* also forms long, yellow needles, and blackening at 230°, intumesces at 273°. The *aurichloride* and *mercurichloride* decompose at 216° and 280° respectively. *Dipyriddytetra-carboxylic acid*, $C_{14}H_{12}N_2(COOH)_4$, is obtained on oxidising tetramethyldipyriddy with potassium permanganate.
M. O. F.

Synthetical Alkines of the Pyridine and Piperidine Series.
By ALBERT LADENBURG [and in part MEISSNER and THEODOR] (*Annalen*, 1898, 301, 117—153).—1-Methylpiperidylalkine [1-methyl-2-hydroxyethylpiperidine], $CH_2 \begin{smallmatrix} CH_2-CH_2 \\ CH_2 \cdot NMe \end{smallmatrix} > CH \cdot CH_2 \cdot CH_2 \cdot OH$, was first prepared by the author (*Abstr.*, 1890, 67) from α -piperidylalkine, the reduction product of α -picolylalkine, obtained by the action of formaldehyde on α -picoline. A substance of the same composition was subsequently obtained by Lipp (*Abstr.*, 1892, 1245), who submitted 1-methyltetrahydropicoline to the action of formaldehyde, and reduced the product; the fact that the two compounds are not identical was ascribed to the presence of impurities in the specimen prepared by Ladenburg. The latter, however, showed that this could not be the true explanation (*Abstr.*, 1893, i, 426), and subsequently suggested the influence of asymmetric nitrogen as the cause of isomerism (*Abstr.*, 1897, i, 437). This view must in turn be abandoned, the author having found that the two alkines are structurally different, the action of formaldehyde on 1-methyltetrahydropicoline yielding 1:2-dimethyl-3-hydroxymethyl- Δ^2 -tetrahydropyridine, $CH_2 \begin{smallmatrix} C(CH_2 \cdot OH) : CMe \\ CH_2 \text{-----} CH_2 \end{smallmatrix} > NMe$, instead of 1-methyl-2-hydroxyethyl- Δ^2 -tetrahydropyridine (*Abstr.*, 1897, i, 229).

A detailed account is given of several compounds described in the author's first paper on this subject (*Abstr.*, 1890, 67), along with new bases of the same type.

1-Ethylpiperidylalkine [1-ethyl-2-hydroxyethylpiperidine],



is prepared by heating piperidylalkine with an aqueous solution of potassium ethyl sulphate; it is a colourless, viscous liquid, which boils at 241.5 (corr.), and has the sp. gr. = 0.9766 at 17°. The *mercurichloride* crystallises in colourless rhombohedra, containing 3H₂O, and melts at 180—181°. The *platinochloride* of the ethylammonium base crystallises in small, orange prisms, and melts at 210°.

1:2-Ethylvinylpiperidine, $CH_2 \begin{smallmatrix} CH_2 \cdot NEt \\ CH_2 \cdot CH_3 \end{smallmatrix} > CH \cdot CH : CH_2$, is obtained

by heating a solution of the alkine in glacial acetic acid with concentrated sulphuric acid at $175-180^{\circ}$; it boils at $173-178^{\circ}$ under a pressure of 754 mm. The *platinochloride* melts at 205.5° .

Propylpipecolylalkine [2-hydroxyethyl-1-propylpiperidine], $C_{10}H_{21}NO$, is a viscous liquid which boils at 246° , and does not solidify at -14° ; it has a sp. gr. = 0.9578 at $20^{\circ}/4^{\circ}$. The *mercurichloride* and *platinochloride* of the methylammonium base melt at 157° and 194.5° respectively. 1-*Isopropylpipecolylalkine* [2-hydroxyethyl-1-isopropylpiperidine] boils at $235-239^{\circ}$, and has a sp. gr. = 0.9597 at 20° ; the *mercurichloride* and *platinochloride* of the methylammonium base melt at 198° and 182° respectively.

1-*Benzylpipecolylalkine* [1-benzyl-2-hydroxyethylpiperidine], $C_{14}H_{21}NO$, boils at $318-321^{\circ}$, and has a sp. gr. = 1.0343 at 4° . 1-*Methylpipecolylmethylalkine* [1-methyl-2- β -hydroxypropylpiperidine], $C_9H_{19}NO$, is a strongly alkaline liquid which solidifies in liquid air, and melts in solid carbonic anhydride; the *mercurichloride* and *platinochloride* melt at $150-155^{\circ}$ and $203-204^{\circ}$ respectively.

1:3-*Methylethylpiperidine*, $C_8H_{17}N$, is prepared by reducing with tin and hydrochloric acid the base erroneously described by Lipp as methylvinylpiperidine (Abstr., 1897, i, 230); it is a colourless liquid having the odour of piperidine, boils at 153.1° (corr.) under a pressure of 756 mm., and has a sp. gr. = 0.8394 at 0° . The *hydrochloride* crystallises in long, colourless prisms, and melts at $174-176^{\circ}$; the *aureichloride* forms needles, and melts at $104-105^{\circ}$. Distillation of the hydrochloride in an atmosphere of hydrogen chloride yields β -ethylpiperidine, from which β -pyridine is obtained on distilling the hydrochloride with zinc dust.

M. O. F.

Hydrogenisation of Nicotyrine. By AMÉ PICTET and PIERRE CRÉPIEUX (*Ber.*, 1898, 31, 2018—2022).—The authors endeavour to accomplish the final stage in the synthesis of nicotine by the partial hydrogenisation of nicotyrine, the methiodide of which has been synthetically prepared (Abstr., 1895, i, 627).

Iodonicotyrine, produced on shaking nicotyrine with a solution of iodine in dilute soda, acidifying with acetic acid, and again rendering alkaline, separates in colourless needles, and can be purified by distillation with steam; it melts at 110° , and dissolves readily in alcohol, benzene, and ether. Its alcoholic solution produces a green coloration with pine-wood moistened with hydrochloric acid. Like nicotyrine, it is a monacidic, tertiary base; the *picrate* melts at 124° , the *platinochloride* at 171° , the *mercurichloride* at 155° , and the *methiodide* at $196-197^{\circ}$.

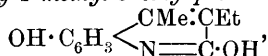
Dihydronicotyrine (1-methyl-2-pyridyldihydropyrroline), resulting from the reduction of *iodonicotyrine* with zinc and hydrochloric acid, is a liquid boiling at 248° (corr.) which in all its properties greatly resembles nicotine; it is strongly alkaline, and behaves as a diacidic base. The *platinochloride*, $C_{10}H_{12}N_2 \cdot H_2PtCl_6$, has no definite melting point, the *picrate* melts at 156° ; the *methiodide* does not crystallise, but the corresponding *platinochloride*, $C_{10}H_{12}N_2 \cdot Me_2PtCl_6$, melts at $240-242^{\circ}$. The base gives no colour reaction with the pine-wood, but decolorises permanganate in acid solution.

The authors have not succeeded in obtaining nicotine from nicotine.
G. T. M.

Derivatives of 3'-Ethyllepiline (4'-Methyl-3'-ethylquinoline).
By HENDRICK BYVANCK (*Ber.*, 1898, 31, 2143—2154).—(2 or 4)-

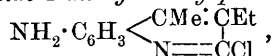
Amido-2'-hydroxy-4'-methyl-3'-ethylquinoline, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CMe} \cdot \text{CEt} \\ \diagdown \quad \diagup \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$
obtained by heating together metaphenylenediamine and ethylic ethyl-acetoacetate in sealed tubes at 165—170°, crystallises in fine, shining, colourless needles, and melts and decomposes at 277—284°; it is sparingly soluble in benzene and ether, but dissolves readily in ethylic and methylic alcohols, yielding solutions with a beautiful, blue fluorescence. It possesses both basic and acidic properties, dissolves readily in dilute sulphuric acid, and is reprecipitated by sodium carbonate. The *hydrochloride* crystallises in radiate groups of needles; the nitrate in hard prisms; and the *cadmiochloride* in bundles of long needles; the *zincochloride* and *mercurichloride* crystallise in brownish prisms. Ferric chloride produces a brown precipitate in solutions of the base.

(2 or 4)-2'-Dihydroxy-4'-methyl-3'-ethylquinoline,



is formed on heating a solution of diazohydroxyethyllepiline; its salts readily dissociate on treatment with water. It is insoluble in ether, slightly soluble in benzene and light petroleum, but dissolves readily in methylic and ethylic alcohols. It separates from chloroform, in which it is somewhat sparingly soluble, in white needles, and melts and decomposes at 263—273°.

2'-Chloro-(2 or 4)-amido-4'-methyl-3'-ethylquinoline,



is produced when the hydrochloride of amidohydroxyethyllepiline, heated with phosphorus oxytrichloride at 135—140° during 2½—3 hours, is purified by precipitation with ammonia and crystallisation from light petroleum, when it forms slender, white needles and melts sharply at 138°. It dissolves readily in methylic and ethylic alcohols, giving solutions with a blue fluorescence, and is readily soluble in benzene. Its salts, with hydrochloric, nitric, and sulphuric acids, form solutions having a beautiful, green fluorescence. The *picrate* crystallises in plates, and the *chromate* is sparingly soluble; of its double salts, that with mercuric chloride forms prisms, whilst that with zinc chloride is obtained in oily drops which solidify to yellow flocks. The hydrochloride, when treated with gold chloride, gives a precipitate of metallic gold.

(2 or 4)-Amido-4'-methyl-3'-ethylquinoline, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CMe} \cdot \text{CEt} \\ \diagdown \quad \diagup \\ \text{N} = \text{CH} \end{smallmatrix}$, is

most readily prepared by heating amidochlorethyllepiline with hydriodic acid, potassium iodide, and phosphorus. The free base separates from ether, on the addition of light petroleum, in beautiful, colourless, prismatic crystals, melts at 84°, is readily soluble in alcohol, methylic alcohol, benzene, ether, and chloroform, less so in water, and sparingly in light petroleum. Its aqueous solution exhibits a blue fluorescence.

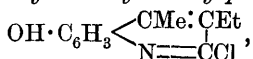
The *picrate* forms yellow flocks or fine yellow needles. The *hydriodide*, $C_{12}H_{14}N_2.HI$, decomposes at 260° and melts at 276° .

(2 or 4)-*Hydroxy-4'-methyl-3'-ethylquinoline*, $OH \cdot C_6H_3 \begin{smallmatrix} \text{CMe} \cdot \text{CEt} \\ \text{N} = \text{CH} \end{smallmatrix}$, obtained by the action of nitrous acid on the foregoing base, has phenolic properties, forms colourless crystals, and melts at 189° .

(2 or 4)-*Amido-4'-methyl-3'-ethylquinolinesulphonic acid*, formed by heating amidoethyllepidine with fuming sulphuric acid on the water bath, crystallises in beautiful, yellow needles which melt above 300° , and appear to be anhydrous; calcium acetate and barium chloride produce no precipitate in its solution. It may be oxidised by potassium permanganate, and the product has the properties of a strong acid, giving a *barium* salt which does not dissolve even in strong hydrochloric acid, and a greenish-blue *copper* salt; the latter, when decomposed with hydrogen sulphide, gives a *substance* which crystallises from water in white needles, and whose aqueous solution is coloured intensely yellow by ferric chloride.

4'-*Methyl-3'-ethylquinoline*, $C_6H_4 \begin{smallmatrix} \text{CMe} \cdot \text{CEt} \\ \text{N} = \text{CH} \end{smallmatrix}$, is made from amidoethyllepidine by reducing its diazo-compound with stannous chloride and decomposing the hydrazine with copper sulphate. The *platinochloride*, $(C_{12}H_{13}N)_2.H_2PtCl_6$, crystallises in yellow, shining leaflets, and melts and decomposes at $196-200^\circ$; the *picrate* forms yellow needles and melts at 202° .

2'-*Chloro-(2 or 4)-hydroxy-4'-methyl-3'-ethylquinoline*,



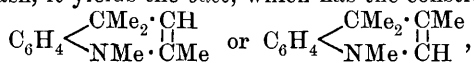
prepared from amidochlorethyllepidine by the diazo-reaction, has marked acidic properties, and dissolves very sparingly in ether, but is more soluble in ethylic and methylic alcohols; it melts sharply at 227° ; the *hydrochloride* forms long, reddish-yellow needles, and dissociates on addition of water. It is not reduced when heated with a mixture of hydriodic acid, potassium iodide, and amorphous phosphorus, but forms a *hydriodide* which is sparingly soluble in water. When oxidised with potassium permanganate, it yields 2-chloro-4-methyl-3-ethylpyridine-5:6-dicarboxylic acid, $\begin{smallmatrix} \text{CCl} = \text{N} - \text{C} \cdot \text{COOEt} \\ | \\ \text{Cet} \cdot \text{CMe} \cdot \text{C} \cdot \text{COOEt} \end{smallmatrix}$, which forms beautiful, white crystals, and dissolves readily in water, alcohol, and ether; its aqueous solution gives a yellow coloration on the addition of ferrous sulphate, and a yellowish cloud with ferric chloride.

2'-*Iodolepidine*, $C_6H_4 \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{N} = \text{CI} \end{smallmatrix}$, may be obtained by heating the corresponding chlorolepidine with a mixture of hydriodic acid, potassium iodide, and amorphous phosphorus; it crystallises from light petroleum in long, colourless needles, melts at 90° , and dissolves readily in ether, methylic and ethylic alcohols, and light petroleum. Its *hydrochloride* and *hydriodide* crystallise in needles, and are sparingly soluble in water. It is easily reduced to lepidine by iron filings and sulphuric acid.

A. L.

Action of Methyl iodide on Trimethyldihydroquinoline from Indole. Tetramethyldihydroquinoline. By ANTONIO PICCININI (*Gazzetta*, 1898, 28, i, 187—196).—Zatti and Ferratini (*Abstr.*, 1890, 1292) obtained a pentamethyldihydroquinoline by the action of methyl iodide on the trimethyldihydroquinoline recently examined by Ciamician and Piccinini (*Abstr.*, 1897, i, 101); it is now shown that a tetramethyldihydroquinoline is formed in one stage of the reaction.

Tetramethyldihydroquinoline hydriodide, $C_{18}H_{17}N \cdot HI$, is prepared by heating the trimethyldihydroquinoline with methyl iodide at 90° in an autoclave for 3 hours; the excess of methyl iodide is evaporated, and the tetramethyl-derivative separated from the tri- and pentamethyl derivatives by washing with acetic acid and treatment with alcohol. It forms lustrous, colourless scales melting at $227\text{--}228^\circ$, is stable when pure, and may be crystallised from water. On treatment with cold potash, it yields the *base*, which has the constitution



and is a highly refractive, colourless oil, boiling at $170\text{--}171^\circ$ under 30 mm. pressure; under the ordinary pressure, it boils at 260° , with decomposition. The *picrate*, $C_{13}H_{17}N \cdot C_6H_2(NO_2)_3 \cdot OH$, crystallises in lustrous, yellow, laminæ melting at $107\text{--}108^\circ$.

Benzoyltetramethyldihydroquinoline, $C_{13}H_{16}N \cdot CPh$, is obtained by heating the base, suspended in potash, with benzoic chloride; it forms small, colourless, rhomb-shaped laminæ melting at 102° . *Benzoyltrimethyldihydroquinoline* crystallises in lustrous, yellow scales melting at $137\text{--}138^\circ$.

Tetramethyltetrahydroquinoline, $C_{13}H_{19}N$, obtained as an oil by reducing the dihydroquinoline with zinc and hydrochloric acid, does not redden on exposure to air; the *picrate*, $C_{13}H_{19}N \cdot C_6H_2(NO_2)_3 \cdot OH$, crystallises in small, yellow prisms melting at $148\text{--}149^\circ$. The *methiodide*, $C_{13}H_{19}N \cdot MeI$, prepared by heating the base with methyl iodide at 100° , crystallises in colourless prisms, and volatilises at 240° without previously melting. On distilling tetramethyltetrahydroquinoline with hydriodic acid in a current of hydrogen, methyl iodide is eliminated, but the base formed was not obtained pure.

W. J. P.

Pyrazolecarboxylic Acids. By LUIGI BALBIANO (*Gazzetta*, 1898, 28, i, 382—390).—Claisen (*Abstr.*, 1897, i, 440) has synthesised

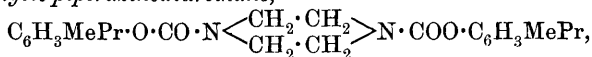
1-phenylpyrazole-4:5-dicarboxylic acid, $N \begin{array}{c} \text{NPh} \cdot \text{C} \cdot \text{COOH} \\ \diagup \quad | \\ \text{CH} - \text{C} \cdot \text{COOH} \end{array}$, which melts at $215\text{--}216^\circ$ and gives a dimethylic salt melting at $75\text{--}76^\circ$. Balbiano and Severini (*Abstr.*, 1893, i, 673) also prepared an acid to which they assigned this constitution, but the properties of which are different.

On repeating the previous work, the author finds that, on oxidising 1-phenylmethylethylpyrazole, 1-phenylpyrazole-3:4-dicarboxylic acid, melting at 234° , is obtained; its dimethylic salt crystallises in lustrous tablets melting at $97\text{--}98^\circ$ (compare *Abstr.*, 1893, i, 673). On

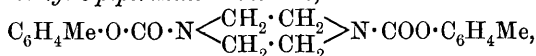
oxidising 1-phenyldimethylpyrazole as before, 1-phenyl-3-methylpyrazole-4-carboxylic acid is obtained; this crystallises in needles melting at 194—195°, and when heated gives 1-phenyl-3-methylpyrazole. From the mother liquors of its preparation, however, 1-phenyl-5-methylpyrazole-4-carboxylic acid, melting at 166—168°, was separated. The acid described by Balbiano and Severini as melting at 134° was a mixture of the two acids melting at 194—195° and at 166—168°; and the supposed 1-phenyl-3:4-dimethylpyrazole contained 1-phenyl-4:5-dimethylpyrazole. The erroneous constitution assigned by Balbiano and Severini was due to working with this mixture. W. J. P.

Aromatic Diurethanes of Piperazine. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1898, 126, 1802—1805).—*Orthochlorophenylic piperazinediurethane*, $C_6H_4Cl \cdot O \cdot CO \cdot N \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle N \cdot COO \cdot C_6H_4Cl$, obtained by warming an alcoholic solution of piperazine and orthochlorophenylic carbonate in molecular proportion, forms small crystals melting at 165—172°. It is insoluble in water, slightly soluble in alcohol and ether, soluble in benzene and nitrobenzene, and very soluble in chloroform.

Thymylic piperazinediurethane,



obtained in a similar manner from piperazine and thymylic carbonate, forms colourless crystals, melting at 139—140°; it is insoluble in water, slightly soluble in ether, and soluble in benzene and nitrobenzene. *Orthotolylic piperazinediurethane*,



from piperazine and orthotolylic carbonate, forms crystals melting at 135° and is insoluble in water, soluble in alcohol, ether, and nitrobenzene, and very soluble in chloroform and benzene. The corresponding *meta*- and *para*-derivatives melt at 138—139° and 238° respectively, and resemble the ortho-compound in their behaviour with solvents. All these diurethanes, like those previously described, possess great stability, and are not altered by heating with alcoholic ammonia at temperatures below 200°; they are decomposed, however, by heating with concentrated potash at 100° and by ammonia above 200°. When heated with concentrated sulphuric acid, phenylic piperazinediurethane yields orthophenolsulphonic acid in theoretical amount, the remainder of the molecule being apparently completely destroyed. N. L.

Heptatomic Rings Containing Nitrogen: A Correction. By EMIL FISCHER (*Annalen*, 1898, 301, 282—284).—The first compound containing nitrogen in a ring composed of seven atoms is ethylhydrocarbazostyryl, $C_6H_4 \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ NEt \cdot NH \end{smallmatrix} \rangle CO$, prepared by Fischer and Kuzel (*Abstr.*, 1883, 1132). Rupe and Roesler (this vol., i, 573) are not justified, therefore, in ascribing the first member of this series to Busch (*Abstr.*, 1895, i, 31). M. O. F.

The Cyclo-amides: 2'-Ketobenzomorpholine and 2'-Benzoparoxazine Derivatives. By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1898, 20, 555—568).—Whereas the sodium

derivative of 2'-ketobenzomorpholine, $C_6H_4 \begin{smallmatrix} O-CH_2 \\ \diagup \\ NH \cdot CO \end{smallmatrix}$, gives rise, when treated with alkylic iodides, to derivatives of the type $C_6H_4 \begin{smallmatrix} O-CH_2 \\ \diagup \\ NR \cdot CO \end{smallmatrix}$, the silver salt, under similar conditions, produces substances of the type $C_6H_4 \begin{smallmatrix} O \cdot CH_2 \\ \diagup \\ N : C \cdot OR \end{smallmatrix}$, derived from 2'-hydroxybenzoparoxazine. This

behaviour is analogous to that of the sodium and silver salts of the anilides; moreover, acidyl chlorides interact with the silver salt of 2'-ketobenzomorpholine in the same way as with the silver derivatives of the anilides (compare Wheeler and Walden, *Abstr.*, 1897, i, 280), well characterised acyl derivatives being obtained, in which the acidyl group is united to nitrogen; it is noteworthy that Duparc (*Abstr.*, 1887, 948) was unable to obtain an acetyl derivative by heating 2'-ketobenzomorpholine with acetic anhydride at 180°.

The substances of the type $C_6H_4 \begin{smallmatrix} O-CH_2 \\ \diagup \\ NR \cdot CO \end{smallmatrix}$, obtained from the sodium derivative of 2'-ketobenzomorpholine, are very stable, and are only partially decomposed by prolonged heating with concentrated hydrochloric acid, an ortho-alkylamidophenol, $OH \cdot C_6H_4 \cdot NHR$, being formed. The derivatives of the type $C_6H_4 \begin{smallmatrix} O \cdot CH_2 \\ \diagup \\ N : C \cdot OR \end{smallmatrix}$ are, on the other hand, very unstable, 2'-ketobenzomorpholine being produced when they are exposed either to the action of the air or of cold dilute hydrochloric acid; in this, they resemble the isanilides, and, like the latter, they readily interact with bases to form compounds of the type $C_6H_4 \begin{smallmatrix} O \cdot CH_2 \\ \diagup \\ N : C \cdot NHR \end{smallmatrix}$, which yield well-characterised salts.

Since, in general, the behaviour of 2'-ketobenzomorpholine is the same as that of formanilide, the normal structure, $C_6H_4 \begin{smallmatrix} O-CH_2 \\ \diagup \\ NH \cdot CO \end{smallmatrix}$,

is given to it, instead of the enolic formula, $C_6H_4 \begin{smallmatrix} O-CH_2 \\ \diagup \\ N : C \cdot OH \end{smallmatrix}$. In discussing the structure of the amides, the authors point out that, as a rule, they cannot be looked on as possessing an enolic structure, for otherwise their hydroxy-derivatives would give rise, when heated, to imido-lactones, water being separated, as in the case of the hydroxy-acids; thus γ -hydroxyvaleramide, $OH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C(OH) : NH$,

would produce the derivative $\begin{smallmatrix} CH_2-CH_2 \\ | \quad | \\ CH_2 \cdot O \cdot C : NH \end{smallmatrix}$ instead of decomposing with loss of ammonia, as is actually the case. Lachmann's view (*Abstr.*, 1896, i, 601) that acetamide and benzamide contain a hydroxyl group, since they immediately generate hydrogen chloride when brought into contact with phosphorus pentachloride, whereas oxamethane, which undoubtedly contains a carbonyl group, does not do

so under the same conditions, is looked on as erroneous; the difference in behaviour probably depends simply on the amide chlorides produced in the former cases being far less stable, since they are of a more negative character, than that initially produced in the latter.

The *sodium* derivative, $C_6H_4 \begin{smallmatrix} O \cdot CH_2 \\ \diagup \quad \diagdown \\ N : C \cdot ONa \end{smallmatrix}$, of 2'-ketobenzomorpholine is best prepared by adding the latter (5 grams) to a solution of sodium in methylic alcohol, evaporating to dryness, and heating the residue during several hours at 100° under a pressure of 13 mm.; it is immediately decomposed by water, and, when heated with methylic iodide,

gives rise to 1'-methyl-2'-ketobenzomorpholine, $C_6H_4 \begin{smallmatrix} O \text{---} CH_2 \\ \diagup \quad \diagdown \\ NMe \cdot CO \end{smallmatrix}$. The latter is best prepared by dissolving 1.6 grams of sodium in a small quantity of methylic alcohol, and heating the solution with 2'-ketobenzomorpholine (10 grams) and methylic iodide (20 grams) for 7 hours at 135°; it crystallises from alcohol in large, colourless prisms, melts at 58—59°, boils at 156° under a pressure of 14 mm., and is insoluble in alkalis and in cold dilute hydrochloric acid; when heated with concentrated hydrochloric acid at 150—160° during several hours, it yields a small quantity of orthomethylamidophenol. 1'-Ethyl-2'-ketobenzomorpholine, prepared in the same manner as the methyl derivative, is a pale yellow liquid which boils at 157—159° under a pressure of 15 mm.

The *silver* derivative of 2'-ketobenzomorpholine, prepared by dissolving the latter in alcohol and adding, first sodium ethoxide (1 mol.), and then the calculated amount of silver nitrate, is a light grey powder which is not affected by light or decomposed by water or alcohol. Phenol, however, immediately reduces it, silver being precipitated; similarly, the silver derivatives of formanilide and of 2:4-dichloroformanilide are decomposed by a solution of phenol in benzene, by aqueous quinol, or alcoholic β -naphthol.

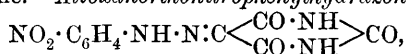
2'-Methoxybenzoparoxazine, $C_6H_4 \begin{smallmatrix} O \cdot CH_2 \\ \diagup \quad \diagdown \\ N : C \cdot OMe \end{smallmatrix}$, prepared by heating the above described silver derivative with methylic iodide (1½ mols.) at 115—120° during 8 hours, is a colourless oil with a characteristic odour, which boils at 135—136° under a pressure of 21 mm., and is immediately decomposed by dilute hydrochloric acid, 2'-ketobenzomorpholine being regenerated. 2'-Ethoxybenzoparoxazine boils at 135—136° under a pressure of 16 mm., whilst the corresponding 2'-isopropyl derivative boils at 137—138° under a pressure of 14 mm., the 2'-isobutyl derivative at 160—164° under a pressure of 21 mm., and the 2'-isoamyl derivative at 174—175° under the same pressure.

The 1'-acetyl derivative, $C_6H_4 \begin{smallmatrix} O \text{---} CH_2 \\ \diagup \quad \diagdown \\ NAc \cdot CO \end{smallmatrix}$, of 2'-ketobenzomorpholine, prepared by adding the calculated quantity of acetic chloride to the silver derivative suspended in ether, separates in long, white needles, melts at 77°, and can be recrystallised without change from water. The corresponding benzoyl derivative crystallises from benzene in colourless prisms, and melts at 93°.

2'-Anilidobenzoparoxazine, $C_6H_4 \begin{smallmatrix} O \cdot CH_2 \\ \diagup \quad \diagdown \\ N : C \cdot NHPH \end{smallmatrix}$, prepared by the action of aniline on 2'-ethoxybenzoparoxazine, crystallises in colourless prisms, and melts at 126° ; the *hydrochloride* melts at $220-223^\circ$, the *hydriodide* at $195-196^\circ$, and the *nitrate* at 147° . 2'-*Meta-chloranilidobenzoparoxazine* crystallises from benzene in colourless plates, and melts at $112-114^\circ$; the *hydrochloride*, $C_{14}H_{10}N_2OCl \cdot HCl$, melts and decomposes at $205-207^\circ$. The corresponding β -*naphthylamine* derivative, $C_{18}H_{14}N_2O$, crystallises from benzene in white leaflets, and melts at $154-155^\circ$; the *isobutylamine* derivative yields a *hydrochloride*, $C_{12}H_{16}N_2O \cdot HCl$, which melts at $220-223^\circ$. 2'-*Allyl-amidobenzoparoxazine* crystallises from light petroleum containing benzene, in colourless prisms, and melts at 63° ; its *hydrochloride*, $C_{11}H_{12}N_2O \cdot HCl$, crystallises in colourless needles, and melts at 190° .

W. A. D.

Preparation of Alloxanphenylhydrazone from Barbituric Acid. By OTTO KÜHLING (*Ber.*, 1898, 31, 1972-1977. Compare Abstr., 1892, 442).—Alloxanphenylhydrazone is readily formed by the action of diazobenzene chloride solution on barbituric acid, the product being in every respect identical with that previously obtained by the action of phenylhydrazine on alloxan in acid solution. When the hydrazone is reduced with tin and hydrochloric acid, it yields uramil and aniline. *Alloxanorthonitrophenylhydrazone*,



prepared from barbituric acid by the action of the diazo-chloride derived from orthonitraniline, crystallises in yellow, microscopic needles melting above 310° , has the properties of a feeble acid, and is reduced by tin and hydrochloric acid in the same way as alloxanphenylhydrazone. When boiled with sodium carbonate solution, it is converted into an unstable *substance*, which crystallises in pale yellow, slender needles, melts at $194-196^\circ$, and probably has the constitution, $NO_2 \cdot C_6H_4 \cdot NH \cdot N : CH \cdot CO \cdot NH \cdot COOH$. *Alloxanparanitrophenylhydrazone* forms lustrous, microscopic crystals, melts above 300° , and is converted by sodium carbonate into an unstable, yellow compound of the formula, $C_9N_4H_8O_5$, which melts at $193-194^\circ$. A. H.

Action of Ethylic Chlorofumarate on Amidoximes. By C. WOLF (*Ber.*, 1898, 31, 2110-2112).—When ethylic chlorofumarate is added to an alcoholic solution containing sodium ethoxide and the amide of benzhydroximic acid, benzenylamidoxime, dibenzenylazoxime, and the *sodium* derivative of a *compound* having the formula $C_{13}H_{12}N_2O_4$ are produced. The compound obtained by decomposing the sodium derivative with acids, crystallises from alcohol in lustrous, silky needles, and melts at 154° . It may have either of the following

formulae, $\begin{smallmatrix} CPh \cdot N - O \\ \diagup \quad \diagdown \\ NH \cdot CO \cdot CH \end{smallmatrix} > C \cdot COOEt$ or $\begin{smallmatrix} CPh \cdot N \cdot O \\ \diagup \quad \diagdown \\ NH - CO \end{smallmatrix} > C \cdot CH \cdot COOEt$. This

substance does not yield an additive product with bromine, and its alcoholic solution gives no colour reaction with ferric chloride. The *silver* derivative, $C_{13}H_{11}N_2O_4Ag$, formed by treating its ammoniacal

solution with silver nitrate, melts at 94° , and yields a *methyl* derivative when heated at 100° with an alcoholic solution of methylic iodide. When hydrolysed, the compound, $C_{13}H_{12}N_2O_4$, yields *benzenylamidofumaric-esoanhydridecarboxylic acid*; this is sparingly soluble in the usual solvents, but dissolves readily in dilute alkalis; its alkaline solution decolorises potassium permanganate, and with silver nitrate it forms a silver salt.

Phenylethenylamidoxime and ethylic chlorofumarate give rise to *ethylic phenylethenylamidoximefumaric-esoanhydridecarboxylate*, which melts at 158° , and may have a constitution corresponding with either

$$\begin{array}{ccc} CH_2Ph \cdot C:N \text{---} O & & CH_2Ph \cdot C:N \cdot O \\ | & & | \\ NH \cdot CO \cdot CH & & NH \cdot CO \end{array} > C \cdot COOEt \text{ or } > C:CH \cdot COOEt.$$

G. T. M.

Action of Primary Amines on Dinitrosacyls. By J. BOESEKEN (*Rec. Trav. Chim.*, 1897, **16**, 297—353. Compare Holleman, *Abstr.*, 1893, 205).—When a primary amine reacts with a

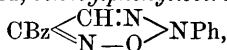
glyoxime peroxide (dinitrosacyl), $\begin{array}{c} R \cdot CO \cdot C:N \cdot O \\ R \cdot CO \cdot C:N \cdot O \end{array}$, one of the acidyl groups is removed as a substituted amide, $R \cdot CO \cdot NHR_1$, whilst the residue combines with a second molecule of the amine, yielding a brown, crystalline product, $R \cdot CO \cdot C \begin{array}{c} \swarrow N-O \\ \searrow CH:N \end{array} > NR_1$, which the author

terms an *isotriazoxole*. When the brown compound is gently heated, it is converted into an isomeric, colourless compound, a *triazoxole*, $R \cdot CO \cdot C \begin{array}{c} \swarrow O \cdot NR_1 \\ \searrow N \cdot CH \end{array} > N$.

Glyoxime peroxides form condensation products with primary amines only; with pyridine, methylaniline, and di-isobutylamine no reaction takes place. Acid groups also appear to interfere with the reaction; sulphanic acid, metanitraniline, and carbamide do not react with glyoxime peroxides; paramidophenol, or one of the naphthylamines, yields amorphous products. A group in the ortho-position relatively to the amido-group of aniline sensibly retards the reaction; for example, meta-xylidene acts very slowly and also incompletely. The reaction takes place more energetically the stronger the base used, thus benzylamine reacts more readily than phenylhydrazine, and the latter than aniline.

The isotriazoxoles are unstable compounds, and attempts to prepare benzoyl or acetyl derivatives proved fruitless. The triazoxoles are more stable, and are characterised by their insolubility in most solvents.

When dibenzoylglyoxime peroxide (5 grams) is boiled for 2 hours with a mixture of aniline (5 grams) and ether (25 grams), benzanilide is deposited, and the oil left after distilling off the ether yields, on the addition of acetic acid, *benzoylphenylisotriazoxole*,



in the form of crystalline needles melting at 97° . The primary product of the action of aniline on dibenzoylglyoxime peroxide is not the brown, crystalline compound, but a substance which could not be obtained in a pure form; it is readily soluble in alkalis, and the alkaline solu-

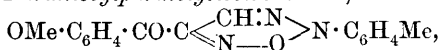
tion has many of the properties of amidoximes, and after a time yields a resin.

Benzoylparatolylisotriazoxole, $C_{16}H_{33}N_3O_2$, crystallises in long, glistening needles, which cannot be recrystallised without undergoing decomposition.

Benzoylanilidoisotriazoxole, $CBz \cdot \begin{smallmatrix} CH:N \\ \diagdown \quad \diagup \\ N-O \end{smallmatrix} \cdot N \cdot NHPh$, obtained from dibenzoylglyoxime peroxide and phenylhydrazine, crystallises on the addition of acetic acid as the *acetate* in red needles; these detonate at 75° , and on exposure to the air lose acetic acid, and become transformed into a yellow powder, the isotriazoxole, which crystallises from methylic alcohol in small, clear yellow needles, decomposing at 65° .

Benzoylbenzylisotriazoxole, crystallising in green needles and decomposing at 112° , and *benzoylbenzylamide*, melting at 106° , are obtained by the action of benzylamine on glyoxime peroxide in ethereal solution. *Benzoylisobutylisotriazoxole* crystallises in green needles. Benzoylisotriazoxole and benzoylethylisotriazoxole could not be obtained in a crystalline form.

Paratoluoylphenylisotriazoxole, $C_6H_4Me \cdot CO \cdot C \cdot \begin{smallmatrix} CH:N \\ \diagdown \quad \diagup \\ N-O \end{smallmatrix} \cdot NPh$, obtained by boiling an ethereal solution of aniline with diparatoluoylglyoxime peroxide, forms brown crystals. *Paratoluoylparatolylisotriazoxole*, decomposing at 125° , and *paratoluoylparatoluidide*, melting at 165° , are obtained from paratoluidine and diparatoluoylglyoxime peroxide. The first products formed are paratoluoylparatoluidide and an *oxime*, $C_6H_4Me \cdot CO \cdot C \cdot (N \cdot OH) \cdot CH:N \cdot N(OH) \cdot C_6H_4Me$, which can be extracted from the ethereal solution by alkalis; it forms small, colourless crystals readily soluble in ether, acetone, or alcohol, and has many of the properties of an amidoxime; it is readily converted by the loss of water, even on treatment with the usual solvents, into paratoluoylparatolylisotriazoxole. A small quantity of *paratoluoylmetaxylylisotriazoxole* is obtained by the action of metaxylylidine on paratoluoylglyoxime peroxide. *Paratoluoylbenzylisotriazoxole*, decomposing at 115° , and *paratoluoylbenzylamide*, melting at 133° , are obtained from benzylamine, and the same glyoxime peroxide. *Paratoluoylanilidoisotriazoxole*, crystallising from a mixture of ether and methylic alcohol in yellow needles, and *paratoluoylphenylhydrazide*, melting at 167° , are obtained from phenylhydrazine and diparatolyldinitrosacyl. *Paranisoylparatolylisotriazoxole*,



crystallises in brilliant, brown needles; *paranisoylbenzylisotriazoxole* crystallises in long, green needles decomposing at 117° , and *paranisoylbenzylamide* crystallises in colourless needles melting at 126° . *Paranisoylanilidoisotriazoxole* crystallises from a mixture of ether and methylic alcohol in small needles decomposing at 97° ; it forms red salts with acetic and hydrochloric acids, but they are unstable. *Paranisoylphenylhydrazide* melts at 179° .

When paratoluoylparatolylisotriazoxole is reduced with stannous chloride and acetic acid, the products are a small quantity of the

isomeric triazoxole, ammonia, methylamine, paratoluidine, and paratoluic acid; with zinc and acetic acid, a much larger quantity of the isomeride is formed, and the same products as when using stannous chloride. With an alkaline solution of stannous chloride, the products are ammonia, paratoluidine, paratoluic acid, the unaltered substance, and a small quantity of oxalic acid. When warmed with an alcoholic solution of sodium methoxide or ethoxide, the isotriazoxole unites with methylic or ethylic alcohol, yielding methylic or ethylic derivatives of the oxime derivative described above; the *methylic* derivative, $C_6H_4Me \cdot CO \cdot C(N \cdot OH) \cdot CH : N \cdot N(OMe) \cdot C_6H_4Me$, forms small crystals soluble in ether, but insoluble in light petroleum.

Isotriazoxoles are converted into their colourless isomerides by boiling with acetic chloride, and when boiled with acetic anhydride and dry sodium acetate are completely decomposed, for example, isotriazoxole yields oxalic and paratoluic acids, ammonia, and acetoparatoluidide. Oxalic and paratoluic acids are also obtained by oxidising the triazoxole with alkaline potassium permanganate.

When boiled with concentrated potassium hydroxide, paratoluoylparatolyisotriazoxole yields a compound in the form of orange-red crystals melting at 188° , and another which is identical with the oxime derivative, $C_{17}H_{17}N_3O_3$, described above. When the isotriazoxoles are heated to 100° , they decompose with detonation; at 50° , no transformation takes place, and even when heated at $60-70^\circ$ for 12 hours but little of the colourless isomeric triazoxoles are formed. The transformation takes place much more readily in solution, for example, in alcohol, acetic chloride, or glacial acetic acid. Acetic chloride especially appears to facilitate the transformation.

Paratoluoylphenyltriazoxole, $C_6H_4Me \cdot CO \cdot C \begin{smallmatrix} \diagup O \cdot NPh \\ \diagdown N-CH \end{smallmatrix} N$, obtained by boiling the corresponding isotriazoxole with an excess of alcohol (97 per cent.) until the mass becomes colourless, crystallises from glacial acetic acid and melts at 211° .

Paratoluoylparatolytriazoxole melts at 208° .

Paratoluoyltriazoxole, obtained by heating diparatolyglyoxime peroxide with concentrated alcoholic ammonia, melts at 165° .

Paranisoyltriazoxole, $C_{10}H_9N_3O_3$, obtained by heating diparanisoylglyoxime peroxide for 2 hours in sealed tubes with alcoholic ammonia, crystallises from alcohol in colourless needles melting at 144° . *Paranisoylbenzyltriazoxole*, obtained from the iso-compound by boiling with glacial acetic acid, crystallises in needles melting at 190° .

Paratoluoylparatolyltriazoxole is not altered either by boiling with stannous chloride in acid solution, or by zinc dust and acetic acid. When heated with acetic anhydride and anhydrous sodium acetate, it is decomposed, yielding ammonia together with oxalic and paratoluic acids. Paratoluoyltriazoxole, when heated with acetic anhydride and sodium acetate, yields an *acetyl* derivative, $C_{12}H_{11}N_3O_3$, melting above 260° . When heated at 180° with concentrated hydrochloric acid, the triazoxole is completely decomposed into carbonic anhydride, ammonia, paratoluic acid and paratoluidine; it is not decomposed when boiled with potassium permanganate unless the boiling is continued for 24 hours, when an acid, probably terephthalic, is formed.

Paratolyltriazoxole, $\text{N} \begin{smallmatrix} \text{CH} \cdot \text{O} \\ \text{CH} \cdot \text{N} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$, is obtained as its *potassium* salt when paratoluoylparatolyltriazoxole is gently heated with about ten times its weight of concentrated potassium hydroxide until it is completely dissolved; it is separated from the potassium paratoluate, which is also formed, by digestion with alcohol; the free paratolyltriazoxole cannot be recrystallised, as it undergoes decomposition. It is readily soluble in alcohol, acetone, or ether, sparingly in acetic acid, and melts and decomposes at 138° . Paratolyltriazoxole, when boiled with dilute acetic or dilute hydrochloric acid, is decomposed into carbonic anhydride, paratoluidine, and cyanamide, according to the equation $\text{C}_9\text{H}_9\text{N}_3\text{O} + \text{H}_2\text{O} = \text{C}_7\text{H}_7\text{NH}_2 + \text{CO}_2 + \text{CN}_2\text{H}_2$.

Phenyltriazoxole, $\text{CH} \begin{smallmatrix} \text{N} - \text{CH} \\ \text{O} \cdot \text{NPh} \end{smallmatrix} \text{N}$, obtained in the form of its *potassium* salt by boiling paratoluoylphenyltriazoxole with potassium hydroxide, melts at $110-120^\circ$. The potassium salt is unstable and decomposes when recrystallised; its *ammonio-silver* salt, $\text{C}_8\text{H}_6\text{N}_3\text{OAg} + \text{NH}_3$, crystallises well, and when heated at 70° evolves ammonia and yields the *silver* salt, $\text{C}_8\text{H}_6\text{N}_3\text{OAg}$. Phenyltriazoxole is readily decomposed into carbonic anhydride, aniline, and cyanamide, boiling with water being sufficient to bring about the decomposition.

J. J. S.

Alloxuric Bases Present in Urine. By MARTIN KRÜGER and GEORG SALOMON (*Zeit. physiol. Chem.*, 1898, 24, 364—394).—The investigation of the xanthine and hypoxanthine fractions of the alloxuric bases obtained from 10,000 litres of human urine (Abstr., 1896, ii, 200) is described. The former, consisting of 22.2 grams, and not 13 grams as formerly stated, was found to contain 11.36 grams of heteroxanthine, 1.3 grams of paraxanthine, 3.88 grams of xanthine, and 5.14 grams of a new methylxanthine. Paraxanthine is separated from its congeners by extracting with water in which it is easily soluble, whilst heteroxanthine is easily isolated by means of its sparingly soluble sodium derivative; a separation, however, of xanthine from the new methylxanthine could not be effected in this fraction.

The *platinochloride*, $(\text{C}_7\text{H}_8\text{N}_4\text{O}_2)_2 \cdot \text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$, of paraxanthine separates from water in orange crystals belonging to the anorthic system; $a : b : c = 0.8066 : 1 : 1.30098$; $\alpha = 80^\circ 30'$; $\beta = 88^\circ 13'$; $\gamma = 94^\circ 27'$ (Arzruni).

The hypoxanthine fraction contained xanthine, hypoxanthine, adenine, epiguanine, and the new *methylxanthine*, $\text{C}_8\text{H}_6\text{N}_4\text{O}_2$; 2.5 grams of the latter was isolated in a pure state, but it was found impossible to separate the remainder from xanthine. It is obtained from water as a colourless, dull, crystalline powder, and is easily soluble in ammonia, caustic soda, and dilute mineral acids; its *aurochloride* crystallises in lustrous plates, and its *platinochloride* in stellar aggregates of needles. The new substance gives Fischer's xanthine reaction (*Ber.*, 1897, 2236, note), and, with silver nitrate, yields a well-defined *additive* compound which cannot be distinguished in appearance or solubility from that obtained from xanthine; the new base is, by

exclusion, probably a 1-methylxanthine (compare Fischer and Ach, following abstract).

The bases of the hypoxanthine fraction were separated by taking advantage of the difference in the solubilities of their lead derivatives; xanthine, and 1-methylxanthine were precipitated by basic lead acetate, whilst from the filtrate 1-methylxanthine (free from xanthine), hypoxanthine, and a small quantity of adenine were thrown down on adding ammoniacal lead acetate. The remainder of the adenine and the whole of the epiguanine were obtained from the second filtrate by the addition of an ammoniacal solution of silver. The adenine was characterised by its hydrochloride, sulphate, and picrate; the last two salts were analysed; the picrate is anhydrous, and does not contain $1\text{H}_2\text{O}$ as stated by Bruhns (Abstr., 1890, 534). Hypoxanthine was characterised by its hydrochloride and picrate, both of which were analysed; whilst epiguanine was recognised only by qualitative tests.

W. A. D.

Further Syntheses of Xanthine Derivatives from Methylated Uric Acids. By EMIL FISCHER and FRIEDRICH ACH (*Ber.*, 1898, 31, 1980—1988. Compare Abstr., 1897, i, 641).—Only those methyl derivatives of uric acid which contain two methyl groups in the alloxan nucleus are converted by treatment with the chlorides of phosphorus into xanthine derivatives, uric acid itself, and such of its methyl derivatives as have not this constitution, being thereby converted into purine derivatives. When, however, these methyluric acids are treated with phosphorus oxychloride alone, they yield xanthine derivatives.

8-Chloro-3-methylxanthine, $\begin{array}{c} \text{NH}\cdot\text{CO}-\text{C}\cdot\text{NH} \\ | \qquad | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}-\text{N} \end{array} \gg \text{CCl}$, is formed

when 3-methyluric acid (α -methyluric acid) is heated with phosphorus oxychloride, and the product, after the removal of the excess of oxychloride, treated with alcohol. It crystallises in lustrous, flat prisms containing $1\text{H}_2\text{O}$, and decomposes and froths up at $340\text{--}345^\circ$. The sodium, ammonium, and barium derivatives all crystallise in slender needles, whilst the silver derivative is a gelatinous precipitate which is not decomposed by boiling water. 8:3-Chloromethylxanthine is readily converted by methylation, by means of methylic iodide or potassium methyl sulphate, into chlorotheobromine, $\text{C}_7\text{H}_7\text{N}_4\text{O}_2\text{Cl}$, which crystallises in short, lustrous prisms or fascicular groups of needles melting at 304° (corr.). It dissolves in about 250 parts of boiling water and forms crystalline sodium, ammonium, and barium derivatives. It is almost quantitatively converted into theobromine by hydriodic acid, whilst on treatment with methylic iodide and caustic potash, it yields caffeine. The compound obtained from chloromethylxanthine is identical with that prepared directly from theobromine by the action of chlorine or chloride of iodine. The formation of theobromine from α -uric acid shows that the latter is a 3-methyluric acid, since it is known to contain the methyl group in the alloxan nucleus.

3-Methylxanthine, $\begin{array}{c} \text{NH}\cdot\text{CO}-\text{C}\cdot\text{NH} \\ | \qquad | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}-\text{N} \end{array} \gg \text{CH}$, obtained by the reduction of chloromethylxanthine with hydriodic acid and phosphonium

iodide, crystallises in slender, lustrous needles, which gradually decompose above 360° without melting. It dissolves readily in alkalis, and yields crystalline salts. It also yields salts with acids; the *hydrochloride* crystallises in slender needles, the *hydriodide* in compact prisms, and the *nitrate* also forms compact crystals. It yields a crystalline precipitate with silver nitrate, whereas ammoniacal silver oxide produces a white, amorphous precipitate; like all xanthine derivatives, it gives the murexide reaction. This compound is quite distinct from the methylxanthine found by Krüger and Salomon (preceding abstract) in urine. 3-Methylxanthine is converted by methylation into theobromine or caffeine according to the amount of methylic iodide employed.

3:7-Dimethyluric acid is directly converted into chlorotheobromine by treatment with phosphorus oxychloride, a yield of 90 per cent. of the theoretical being obtained.

In addition to the four monomethyluric acids of known constitution, a fifth, termed δ -uric acid, has also been described and must, according to the authors, be regarded as a chemical individual. The formula at present accepted for uric acid does not admit of the existence of five isomerides of this methyl derivative, and it seems probable that the isomerism may be of a geometrical character. A. H.

Bromine Derivatives of Morphine. By HENRI CAUSSE (*Compt. rend.*, 1898, 126, 1799—1802).— *α -Tetrabromomorphine hydrobromide*, obtained by the action of bromine on morphine in presence of concentrated hydrobromic acid, forms colourless crystals melting at 218° . Its molecular weight, determined cryoscopically, was found to be 678 (theory, 682). It is insoluble in cold water, methylic alcohol, and chloroform, but fairly soluble in boiling water and ethylic alcohol; the solutions are optically active. Sodium ethoxide and silver oxide remove part of the bromine, and a *substance* is formed which crystallises in yellow needles and has the properties of a quinone. When boiled with soda, it blackens, and an alkaline gas having the odour of methylamine is evolved; the residue, when acidified and extracted with ether, yields phenol. *β -Tetrabromomorphine hydrobromide* is obtained by adding bromine to a solution of morphine in chloroform, ether, or water, and subsequently digesting the product with dilute sodium thiosulphate solution, and also by cautiously adding hydrogen peroxide or potassium permanganate to the liquid from which the isomeric α -compound has crystallised. It forms infusible yellow, crystals, insoluble in cold water, but soluble in all proportions in methylic alcohol, ethylic alcohol, and acetone. Silver oxide removes the whole of the bromine, with formation of an amorphous, brown *substance*. When treated with boiling soda, it is completely destroyed and yields traces of phenol. *Tetrabromomorphine*, $C_{17}H_{15}Br_4NO_3 + 2H_2O$, is obtained by precipitating the aqueous solution of the α -hydrobromide with sodium carbonate and recrystallising the precipitate from alcohol. It is difficult to obtain perfectly colourless, and is usually of a blue or violet tint. It has both acid and basic functions. The *sulphate* and the *oxalate* of tetrabromomorphine are colourless, crystalline salts, insoluble in water, alcohol, and ether. When baryta water, or an

ammoniacal solution of barium chloride, is added to an aqueous solution of α -tetrabromomorphine hydrobromide, a compound of the formula $C_{17}H_{15}Br_4NO_3 \cdot \frac{1}{2}BaO + H_2O$ is produced. It forms small, colourless crystals, insoluble in water, but soluble in alcohol and acetone. *Tribromomorphine hydrobromide* is contained in the mother liquor obtained in the preparation of α -tetrabromomorphine hydrobromide; it forms crystals, melting at 178° , which are difficult to obtain free from colour. When treated with baryta water, an amorphous, green powder of variable composition is produced. N. L.

Electrolytic Preparation of Hydrocotarnine. By ERICH BANDOW and RICHARD WOLFFENSTEIN (*Ber.*, 1898, 31, 1577—1578).—Cotarnine, $C_{12}H_{15}NO_4$ (30 grams), is dissolved in dilute sulphuric acid (1:5; 170 grams), and the solution is electrolysed until, after some 4 hours, it has become colourless, and with ammonia, a sample gives a pure white precipitate having the melting point of hydrocotarnine, $C_{12}H_{15}NO_3$. The electrodes are of platinum foil, the anode being immersed in dilute sulphuric acid; the current density at the cathode is about 3.5 ampères, and the E.M.F. about 5.3 volts. Crude cotarnine may be used, as obtained from the mother liquor after narcotine has been treated with manganese dioxide and sulphuric acid and the opianic acid has been separated; even in this case, the hydrocotarnine obtained is pure.

Hydrastinine, $C_{11}H_{13}NO_3$, may be converted into hydrohydrastinine, $C_{11}H_{13}NO_2$, in a similar manner. C. F. B.

Condensation of Aldehydes with Hydrocotarnine. By JULIUS KERSTEN (*Ber.*, 1898, 31, 2098—2103. Compare Abstr., 1896, i, 264).—As hydrocotarnine is not acted on by fuming hydrochloric acid at ordinary temperatures, the agent may accordingly be employed in effecting condensations between this base and various aldehydes. Isonarcotine is obtained by mixing together the above base and opianic acid, in molecular proportion, in the presence of fuming hydrochloric acid, and warming the mixture for some time at 60 — 70° .

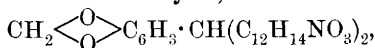
Under similar conditions, combination takes place between metanitrobenzaldehyde and hydrocotarnine, in molecular proportion, unaccompanied by the elimination of water. The compound,

$NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot C_{12}H_{14}NO_3$, melts at 170 — 171° , is soluble in alcohol, benzene, and chloroform, but insoluble in ether, petroleum, and solutions of the alkalis and alkali carbonates, and forms a green solution with concentrated sulphuric acid. The *platinochloride* and the *aurochloride* are insoluble, the former being yellow, and the latter brown. The salts of the base with halogen acids are soluble in water.

Combination occurs between 2 molecules of salicylaldehyde and 1 of the base without elimination of water, the compound produced being insoluble in ether, benzene, chloroform, petroleum, and alkaline solutions, but soluble in alcohol and salicylaldehyde; its *platinochloride* is a red, flocculent precipitate.

Benzaldehyde and hydrocotarnine, in the presence of hydrochloric acid, condense to form the base, $C_6H_5 \cdot CH(C_{12}H_{14}NO_3)_2$, water being eliminated (*Abstr.*, 1896, i, 711). The condensation product crys-

tallises from dilute alcohol in white needles melting at 229—230°, and is soluble in benzene, chloroform, and benzaldehyde, but insoluble in ether, petroleum, and alkaline solutions. The *platinochloride*, $(C_{31}H_{34}N_2O_6)_2H_2PtCl_6$, is obtained in yellow flakes. Piperonal behaves in a similar manner to benzaldehyde; the *base* formed,



melts at 202°, and yields an insoluble, yellow *platinochloride*.

Cinnamaldehyde also combines with 2 molecular proportions of hydrocotarnine, but no elimination of water occurs in the presence of strong hydrochloric acid; the *base* thus produced melts and decomposes at 228—230°, and yields an insoluble, yellow *platinochloride*. When 73 per cent. sulphuric acid is employed instead of hydrochloric acid, the condensation of 2 molecules of hydrocotarnine and 1 of the aldehyde is accompanied by elimination of water; the compound thus obtained, $CHPh \cdot CH \cdot CH(C_{12}H_{14}NO_3)_2$, melts at 139—140°, and yields a *platinochloride*, $(C_{33}H_{36}N_2O_6)_2H_2PtCl_6$.

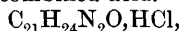
The above condensation products, when dissolved in strong sulphuric acid, exhibit distinctive colorations. G. T. M.

Strychnine. By JULIUS TAFEL (*Annalen*, 1898, 301, 285—348. Compare Abstr., 1892, 1012).—When a current of 5 ampères at a potential of 3·5 volts, is passed through a solution of 30 grams of strychnine in 180 grams of concentrated sulphuric acid mixed with 120 grams of water, two poisonous bases, strychnidine and tetrahydrostrychnine, are produced. After 10 hours treatment, the colourless liquid is diluted with 4 times its own volume of water, nearly neutralised with barium carbonate, and, after filtration, treated with a slight excess of baryta, which precipitates strychnidine and barium sulphate.

Strychnidine, $C_{20}H_{22}NO \begin{array}{c} \diagup CH_2 \\ \diagdown N \end{array}$, crystallises from alcohol in stellate

aggregates of colourless needles, and sinters at 246° (uncorr.), melting to a brown liquid at 250·5°; in a vacuum, it melts at 252°, forming a colourless solution. Impure specimens of the base crystallise in thin, reddish needles melting at 246—248°. Strychnidine boils at 290—295° under a pressure of 14 mm., the colourless distillate immediately becoming crystalline; it dissolves very sparingly in water, forming a distinctly alkaline solution. The base requires 32 parts of boiling absolute alcohol for dissolution, 120 parts of the solvent being necessary at 20°; it dissolves in 50 parts of boiling 60 per cent. alcohol, and in 14 parts of boiling benzene. Chloroform dissolves it still more readily, and when the solution in 10 parts of this medium is treated with 20 parts of ether, 70 per cent. of the base crystallises in prisms. A 6·4 per cent. solution of the base in chloroform has the specific rotatory power $[\alpha]_D = -8\cdot28^\circ$ at 20°. A solution of strychnidine in concentrated sulphuric acid gives coloration with oxidising agents, but aqueous solutions of its salts, in presence of excess of acid, become intensely red with potassium dichromate, hydrogen peroxide, ferric chloride, or sodium nitrite; concentrated nitric acid produces the same effect when added to the base. In this respect,

it resembles dimethylstrychnine, methylisostrychnic acid (*loc. cit.*), and methyltetrahydroquinoline (kairolin); the highly sensitive character of the ferric chloride reaction is also peculiar to these four compounds. Dimethylaniline, dissolved in hydrochloric acid, gives a yellow coloration with ferric chloride, but the test is less sensitive than in the case of kairolin and strychnidine. When bromine water is added to an acid solution of strychnidine, a pink coloration is developed, gradually deepening to violet-red; on continuing the addition of bromine, a dirty violet solid is precipitated, whilst the liquid becomes colourless. Diazobenzene chloride, when added to an acetic acid solution of strychnidine, produces a yellow azo-compound which forms a magenta-coloured solution in dilute hydrochloric acid. On heating the base with benzaldehyde and zinc chloride, a yellow product is obtained, which, when extracted with water and dissolved in alcohol, gives an intense, malachite-green coloration with ferric chloride. An intense red liquid is obtained on adding sodium nitrite to a concentrated solution of strychnidine in excess of hydrochloric acid, but it rapidly becomes brownish-yellow, and deposits a yellow, micro-crystalline precipitate. Ten per cent. nitric acid decomposes the base when boiled with it, yielding a deep red solution which finally becomes olive green; whilst acetic anhydride and phosphorus pentachloride give rise to indefinite products. Strychnidine has the disagreeable, bitter taste of strychnine and deoxystrychnine; it also resembles these alkaloids in its poisonous properties. Unlike deoxystrychnine, it yields two series of salts, of which those containing one molecular proportion of acid are neutral towards litmus, whilst the others have an acidic action, and readily part with a portion of the combined acid. The *hydrochloride*,



forms slender, colourless needles, and when treated with mercuric chloride yields a gelatinous precipitate which becomes crystalline on boiling; potassium dichromate precipitates slender, pale yellow needles, and develops an intense red coloration in presence of excess of acid. The *dihydrochloride*, $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}, 2\text{HCl}$, crystallises in colourless needles, and is converted into the hydrochloride on crystallisation from water. The *methiodide*, $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}, \text{MeI} + 2\text{H}_2\text{O}$, crystallises from water in aggregates of needles several mm. in length.

Tetrahydrostrychnine, $\text{C}_{20}\text{H}_{22}\text{NO}(\text{NH})\cdot\text{CH}_2\cdot\text{OH}$, crystallises from alcohol in colourless prisms containing one molecular proportion of the solvent, which it retains in a vacuum, but loses completely at 100° , it then melts at 202° to a colourless liquid; the base dissolves in 280 parts of water at 20° , and the solution is strongly alkaline towards phenolphthalein, litmus, and turmeric. Tetrahydrostrychnine dissolves in about 20 parts of boiling alcohol or of boiling benzene, and in 14 parts of boiling 95 per cent. alcohol; it dissolves very readily in chloroform, and is precipitated in microscopic needles on adding ether to this solution. The base resembles strychnidine in its behaviour towards concentrated sulphuric acid and potassium dichromate, but yields a wine-red solution when the hydrochloride is treated with ferric chloride or chromic acid, the latter producing a reddish-brown precipitate in concentrated solutions; sodium nitrite has no action on dilute solutions, and precipitates the hydrochloride of the nitrosamine

from concentrated solutions. Bromine water develops a violet or wine-red coloration in a solution of the hydrochloride, and concentrated nitric acid forms an intense yellow solution, which gradually becomes deep red. Acetic anhydride converts the base into a crystalline acetyl derivative, which, when dissolved in concentrated sulphuric acid and treated with potassium dichromate, develops a beautiful violet coloration. On heating the base with concentrated hydrochloric acid at 100° during 3 hours, or with phosphorus oxychloride, it is resolved into strychnidine, which is also formed in association with iodo-bases when tetrahydrostrychnine is heated on the water bath with hydriodic acid (sp. gr. = 1.96) and phosphonium iodide. Tetrahydrostrychnine *hydrochloride*, $C_{21}H_{26}N_2O_2 \cdot HCl$, forms small, slender needles, and dissolves in less than 3 parts of hot water; 2.5 parts of water are required at 20° , and the solution is neutral towards litmus. The *dihydriodide*, $C_{21}H_{26}N_2O_2 \cdot 2HI + 2H_2O$, crystallises in pyramids, and loses water in a vacuum. The *methiodide*, $C_{21}H_{26}N_2O_2 + MeI + H_2O$, crystallises from hot water in elongated, thin, lustrous needles, and dissolves with difficulty in cold water. The *nitrosamine* is resinous, but yields a *hydrochloride* which crystallises from warm water in yellowish, lustrous prisms; reduction with zinc dust and acetic acid converts it into a base, which slowly reduces boiling Fehling's solution.

Strychnoline, $C_{20}H_{24}N \begin{smallmatrix} \diagup C H_2 \\ | \\ N \end{smallmatrix}$, obtained by reducing deoxystrychnine in amyl alcohol with sodium, crystallises from dilute alcohol in small, colourless needles melting at $175-178^{\circ}$ to a viscous resin; it is scarcely soluble in water, and dissolves sparingly in ether, but alcohol, chloroform, and benzene dissolve it readily. The solutions in dilute hydrochloric and sulphuric acids become reddish, and finally brown, when exposed to air, ferric chloride and potassium dichromate giving magenta-red colorations; sodium nitrite produces a liquid having the colour of eosin. When the base is treated with concentrated sulphuric acid, it becomes deep red, and when gently heated yields a violet solution; the solution in concentrated nitric acid is magenta-red.

Dihydrostrychnoline, $C_{20}H_{26}N \begin{smallmatrix} \diagup C H_2 \\ | \\ N \end{smallmatrix}$, prepared by passing a current of electricity through a solution of deoxystrychnine in 50 per cent. sulphuric acid, crystallises from light petroleum in colourless prisms, melts at 129° , and boils at $267-270^{\circ}$ under a pressure of 16 mm. It is very soluble in organic liquids, but dissolves sparingly in water, yielding a distinctly alkaline solution. A 3 per cent. solution in chloroform has the specific rotatory power $[\alpha]_D = +10.5^{\circ}$. In colour reactions and physiological influence, the base resembles strychnidine. The *hydrochloride*, which crystallises in small needles, dissolves very readily in hot water, but more sparingly in cold; the *nitrate* melts to a colourless liquid at 185° in a vacuum, becoming red at 180° in presence of air. The *methiodide* crystallises from water in white needles, and melts at 265° .

Strychnic and isostrychnic acids are indifferent to reducing agents.

Dinitrostrychnine hydrate, $C_{21}H_{22}N_2O_3(NO_2)_2$, is precipitated in

sulphur-yellow needles when sodium acetate is added to an aqueous solution of the nitrate, and contains $1\text{H}_2\text{O}$, which is removed at 165° ; it is soluble in dilute mineral acids, and in alkalis, being precipitated from its solutions in the latter by carbonic anhydride. Alcoholic potash develops a beautiful, violet coloration, but the substance does not give the strychnine reaction with concentrated sulphuric acid and potassium dichromate. The *nitrate* (cacostrychnine), prepared by heating strychnine with 40 parts of 5 per cent. nitric acid, separates from the latter as a golden yellow, crystalline powder, which chars when heated.

Dinitroisostrychnic acid, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_8(\text{NO}_2)_2$, is a microcrystalline, sulphur-yellow substance, insoluble in water and in alcohol, but forming a red solution in alkalis; the *sulphate* crystallises in golden-yellow prisms; the *nitrate*, obtained by heating isostrychnic acid with 40 parts of 20 per cent. nitric acid during 20 hours, forms a dark yellow, microcrystalline powder, which chars when heated; alcoholic potash develops a violet coloration.

Dinitrostrycholcarboxylic acid, $\text{C}_{10}\text{H}_5\text{N}_3\text{O}_8$, is prepared by heating strychnine with 40 parts of 20 per cent. nitric acid during 72 hours in a reflux apparatus, evaporating the liquid to a syrup, and treating this with boiling concentrated nitric acid; it crystallises from concentrated nitric acid in prisms, and from alcohol in needles containing the solvent, which is removed below 110° . It melts at about 300° , liberating carbonic anhydride, and yielding dinitrostrychol; the acid dissolves somewhat readily in hot water, and crystallises in needles. An intense violet coloration is produced when the solution in sodium carbonate is treated with hydrogen sodium sulphite. The *potassium* salt crystallises in pale yellow needles, and detonates without melting when heated; it dissolves in 50 parts of boiling water. The *sodium* salt is more readily soluble, the solution yielding precipitates with lead acetate, and the chlorides of barium, calcium, iron, copper, and cobalt.

Diamidostrycholcarboxylic acid, $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_4$, prepared by reducing dinitrostrycholcarboxylic acid with tin and hydrochloric acid, forms microscopic prisms, dissolving in ammonia, alkalis, and warm hydrochloric acid; the solutions are extremely sensitive towards oxidising agents, and quickly become red or brown when exposed to air. The *hydrochloride* crystallises from hot, hydrochloric acid in colourless prisms.

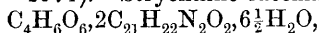
Dinitrostrychol, $\text{C}_9\text{H}_5\text{N}_3\text{O}_6$, produced on heating dinitrostrycholcarboxylic acid with 10 parts of water in sealed tubes at $200\text{--}210^\circ$, crystallises in slender needles; it becomes brown at $250\text{--}270^\circ$, and melts at about 284° , forming a brown liquid which slowly evolves gas. The alcoholic solution is neutral towards methyl-orange, and acid towards litmus. The *potassium* derivative forms minute needles, and the *dibarium* derivative contains $1\text{H}_2\text{O}$; the *methylic ether* is a brownish, crystalline powder, which melts at 196° and sublimes at higher temperatures.

Trinitrostrychol, $\text{C}_9\text{H}_4\text{N}_4\text{O}_8$, is formed from dinitrostrycholcarboxylic acid under the influence of fuming nitric acid, and dissolving somewhat readily in hot water, crystallises in colourless, glistening plates

as the liquid cools ; it becomes brown at 205° , and melts at $215-218^{\circ}$ (uncorr.). The aqueous solution is pale yellow, and has an acid action on litmus and methyl-orange. The *sodium* derivative dissolves very readily in hot water, and much more sparingly in cold water, forming a neutral solution.

M. O. F.

Partial Racemism. By ALBERT LADENDURG and GUIDO DOCTOR (*Ber.*, 1898, 31, 1969—1971).—Strychnine racemate,



differs entirely in its properties from the corresponding salts of dextro- and lævo-tartaric acid, and also from a mixture of these, and is therefore to be regarded as a chemical individual. This is shown by the melting point, water of crystallisation, solubility, and density as given in the following table.

	Sp. gr. at 20° .	Solubility at		Melting point.	Water of crystallisation.
		20°	40°		
Racemate ...	1.4696	2.45	3.69	222°	$6\frac{1}{2}$ molecules
<i>d</i> -Tartrate...	1.5429	2.03	3.10	228	7 ,,
<i>l</i> -Tartrate...	1.6080	1.7	2.05	242	$3\frac{1}{2}$,,

A. H.

Atropine Periodides and Mercuriodides. By HARRY M. GORDIN and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1898, 20, 329—338. Compare Jörgensen, *J. pr. Chem.*, 1871, [ii], 3, 329).—An *enneaiodide*, $\text{C}_{17}\text{H}_{23}\text{NO}_3, \text{HI}, \text{I}_8$, can be obtained under suitable conditions, which are given in detail in the paper. To obtain it in a crystalline form, it is first washed with a little cold alcohol to remove traces of free iodine and then dissolved in warm alcohol, from which it crystallises in dark-green prisms and leaflets ; it is sparingly soluble in ether, chloroform, benzene, or carbon bisulphide, insoluble in water, and is decomposed when heated with water, and also on treatment with concentrated solutions of potassium iodide. At 90° , it begins to give up iodine, and melts to a dark liquid at 140° . One-ninth of the total iodine is firmly combined, whilst eight-ninths is easily removed by reducing agents, such as sulphurous anhydride or sodium thiosulphate.

The periodides are most readily obtained by using chloroform as a solvent. On adding atropine (20 grams) to a warm solution of iodine (30 grams) in chloroform (500 c.c.), the *enneaiodide* crystallises out in shining, dark-green crystals ; the mother liquor gives several successive crops of the dark-blue *pentioidide*, and finally a crop of the brownish-red tri-iodide. The periodides readily give double salts with mercuric iodide ; one may be obtained by shaking the alcoholic solution of the periodide with mercury and gently warming the mixture ; it has the composition $\text{C}_{17}\text{H}_{23}\text{NO}_3, \text{HI}, \text{HgI}_2$, forms yellow crystals, melts at $89-90^{\circ}$, is sparingly soluble in ether or chloroform, moderately in hot water, and very readily in warm alcohol. If a solution of this compound in dilute alcohol is treated with an excess of potassium

iodide, a compound, $(C_{17}H_{23}NO_3, HI)_2HgI_2$, is obtained; it crystallises in white, silky needles melting at $98-99^\circ$, and is readily soluble in warm alcohol or hot water.

The formation of atropine enneaiodide affords a convenient method for estimating the strength of atropine solutions by adding excess of a standard solution of iodine, and titrating back with standard sodium thiosulphate. The method is only successful when extremely dilute solutions of atropine are employed, as otherwise a resinous mass is obtained.
J. J. S.

Soluble Compound of Hydrastine with Monocalcium Phosphate. By THOMAS H. NORTON and H. E. NEWMAN (*J. Amer. Chem. Soc.*, 1897, 19, 838—840).—When hydrastine is triturated with a saturated solution of monocalcium phosphate, a portion of it enters into solution, the amount dissolved increasing with the duration of trituration. At the end of six weeks, the proportion of hydrastine to calcium phosphate corresponds with the formation of a salt of the composition $2Ca(H_2PO_4)_2 \cdot 3C_{21}H_{21}NO_5$. No definite salt could, however, be isolated from the solution, a resinous mass being left on evaporation.
A. H.

Mandragorine. By HERMANN THOMS and M. WENTZEL (*Ber.*, 1898, 31, 2031—2037. Compare Clouzel, *Un. Pharm.*, 1885, 264; Richardson, *Pharm. Journ. and Trans.*, 1888, 938, and 1049; Ahrens, *Abstr.*, 1889, 1074, 1222).—Five grams of Ahrens' alkaloid (m. p. 79°) was dissolved in hydrochloric acid and the solution fractionally precipitated five times with gold chloride, 20 c.c. of a solution of 6 grams of gold chloride in 100 c.c. of water being used for each precipitation. The five fractions thus obtained exhibited, both macroscopically and microscopically, such differences that it was evident that the original alkaloid must have been a mixture. By repeated crystallisation of the different fractions from dilute hydrochloric acid, about 90 per cent. of the original precipitates was obtained in the form of large plates melting at $163-164^\circ$. These proved to be identical in every respect with hyoscyamine aurochloride, and the base obtained from them exhibited all the properties of hyoscyamine.

Mandragorine is thus a mixture of bases, the chief constituent of which is hyoscyamine.
J. J. S.

Preparation of Cholic Acid, and its Behaviour towards Reducing Agents. By FRITZ PREGL (*Pflüger's Archiv.*, 1898, 71, 303—317).—The author describes in detail the method he has found to yield the best results for the preparation of cholic acid from bile. On repeating Destrem's experiments (*Abstr.*, 1879, 333) on the distillation of cholic acid with zinc dust, he found that the product consists of several non-separable hydrocarbons, which are decomposed when distilled under reduced pressure; no definite substance could be obtained by treating the mixture either with bromine or with nitric acid.

On heating cholic acid (0.6 gram) with concentrated hydriodic acid (5 c.c.) and red phosphorus (1 gram) during 8 hours at 270° , a product was obtained which appeared to have the constitution $C_{24}H_{36}$; it was not, however, prepared in at all a pure state.

When a mixture of cholic acid (10 grams), amorphous phosphorus (100 grams), and hydriodic acid (b. p. 127°) is boiled for an hour, a white, pulverulent substance is obtained (compare this vol., i, 389), which readily dissolves in ether, benzene, acetone, and acetic acid, less easily in alkalis and cold alcohol, and is insoluble in water; it cannot be obtained crystalline, but when approximately pure, melts at $117\text{--}120^{\circ}$, and has the composition $\text{C}_{24}\text{H}_{40}\text{O}_2$; the author suggests that it is the monobasic acid, $\text{CH}_3\cdot\text{C}_{20}\text{H}_{31}\text{Me}_2\cdot\text{COOH}$, corresponding to Mylius's formula, $\text{OH}\cdot\text{CH}\cdot\text{C}_{20}\text{H}_{31}(\text{CH}_2\cdot\text{OH})_2\cdot\text{COOH}$, for cholic acid. On adding mineral acids to its alkaline solution and boiling, a coarse-grained precipitate is formed, which appears to consist of an anhydride of the acid analogous to the so-called dyslysins.

On adding the acid $\text{C}_{24}\text{H}_{40}\text{O}_2$ to hot concentrated nitric acid, simultaneous oxidation and nitration occur, an amorphous trinitro-bilianic acid, $\text{C}_{24}\text{H}_{31}\text{N}_3\text{O}_{14}$, being formed, which melts at $169\text{--}172^{\circ}$, dissolves in alkalis with a dark-red coloration, and yields a silver salt, $\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_{14}\text{Ag}_3$. When alcoholic potash is added to its solution in alcohol, a reddish-brown precipitate is produced which dissolves in excess of the alkali; in this respect, trinitro-bilianic acid resembles bilianic acid, and, like the latter, it appears to yield a *phenylhydrazone*, although this is very ill-characterised. W. A. D.

Two Derivatives of Cholic Acid. By FRITZ PREGL (*Pflüger's Archiv.*, 1898, 72, 266—272).—If the crude products of reduction of cholic acid are treated with zinc dust and acetic acid, the presence of the undesirable iodo-compounds is avoided, and the yield of the anhydride, $\text{C}_{48}\text{H}_{78}\text{O}_3$, greatly augmented. It can best be purified by repeated dissolution in alkali and reprecipitation with acid. The substance thus obtained is precipitated from the solution of its potassium salt by carbonic anhydride and exhibits Pettenkofer's bile acids reaction; it melts at $76\text{--}80^{\circ}$, and appears to be identical with Seńkowski's cholylic anhydride (this vol., i, 389), but the author considers that his own method of preparation is to be preferred to Seńkowski's, as the use of hydriodic acid of 127° boiling point ensures comparatively rapid reduction.

In opposition to the view of Seńkowski, the author brings forward evidence to show that the free acid is capable of existence; the precipitate, which is first produced on adding acid to the solution of the anhydride in dilute potash, is flocculent and readily soluble in cold alkali, but if heated cautiously at $50\text{--}60^{\circ}$, it becomes sandy and insoluble; as this change is effected at a temperature far below the melting point of the anhydride, it cannot be due to mere coagulation, but must mean conversion of the free acid into its anhydride.

Further experiments on the action of boiling concentrated nitric acid on the anhydride have given results differing somewhat from those first recorded (*loc. cit.*), and a product crystallising in aggregates of needles has at last been isolated.

Preparation of Bilianic Acid.—The following method of preparing bilianic acid differs from that of Mylius in that it ensures the further transformation of dihydrocholic acid, the intermediate product of oxidation of cholic acid. A mixture of cholic acid (20 grams),

potassium dichromate (40 grams), sulphuric acid (60 grams), and water (160 grams), is heated, as Mylius recommends, until the solution becomes green; the liquid is then cooled, and the product collected over thin gauze and reduced, by rubbing, to a fine state of division; it is once more heated on the water bath for fifteen minutes with a fresh mixture of 20 grams potassium dichromate, 30 grams of sulphuric acid, and 80 grams of water, and it is recommended that, in case any aggregation ensues, the mass should be re-collected and again rubbed down before the oxidation is proceeded with. After cooling, the product is separated, dissolved in excess of soda, digested on the water bath, and filtered from chromium oxide; the filtrate is acidified, and the precipitate of nearly pure bilianic acid collected, washed, dried, and crystallised from dilute acetic acid. In this way, 15—16 grams of bilianic acid, in shining prisms melting at 266° , may be obtained.

Bromine water does not act on bilianic acid at the ordinary temperature, but when heated with it at 110° under pressure, considerable quantities of bromine disappear; the product thus obtained, however, is resinous and unsuited for analysis.

A. L.

Bile Acids. By GOTTHARD BULNHREIM (*Zeit. physiol. Chem.*, 1898, 25, 296—324).—Glycocholic acid can be prepared from ox-bile by shaking it with small amounts of ether and concentrated hydrochloric acid; the acid, which separates after a short time, is washed with water until free from chlorine, and then crystallised first from warm water and afterwards from dilute acetic acid. The yield of pure acid obtained in this way varies from 1.5—2 per cent. of the bile used.

Cholic acid, obtained from glycocholic acid according to Hartmann's directions (*Kolbe's Journal*, 19, 307), forms prismatic crystals containing $1\text{H}_2\text{O}$, which, when placed in alcohol, change to small tetrahedra containing $1\text{C}_2\text{H}_6\text{O}$; the yield is from 62—70 per cent. of the theoretical. The author was unable to prepare cholesteric acid by the oxidation of cholic acid according to Tappeiner's directions (*Abstr.*, 1879, 388).

Bilianic acid, $\text{C}_{24}\text{H}_{34}\text{O}_8 + 2\text{H}_2\text{O}$, obtained by oxidising cholic acid with potassium chromate and sulphuric acid, was purified by dissolving in absolute alcohol, and after treating the solution with hydrochloric acid, allowing it to stand in sunlight for some days. The diethylic bilianate thus formed was hydrolysed with barium hydroxide, and the bilianic acid produced crystallised from alcohol; it is easily soluble in acetic acid, ether, and alcohol, but almost insoluble in light petroleum. The anhydrous acid melts at 264° (uncorr.), and is dextro-rotatory $[\alpha]_{\text{D}} = +76^{\circ}$. The silver salt forms small needles, and the potassium hydrogen salt plates. Bilianic acid is stable towards oxidising agents, chromic acid only attacking it when concentrated and on boiling; hydrogen peroxide, potassium ferrocyanide, and hypobromite, appear to be without action, and a cold solution of potassium permanganate is only reduced after some time. It does not give Pettenkofer's reaction, but on gently warming with concentrated sulphuric acid a peculiar green fluorescence is produced.

Dehydrocholic acid, isolated from the oxidation products of cholic acid, crystallises from dilute acetic acid and melts at 232° . It does

not give Pettenkofer's reaction, but with sulphuric acid a green fluorescence is produced.

Cholanic acid crystallises from acetic acid in quadratic prisms melting at 286° (uncorr.), and is dextrorotatory; $[\alpha]_D = +113^{\circ}$. Its normal ethylic salt gives a *phenylhydrazone* as a radiating, crystalline mass, and therefore cholanic acid must be assumed to be a ketonic acid; it is more stable towards permanganate than bilianic acid, which it otherwise resembles in its reactions.

No crystalline cholesteric acid could be obtained by the oxidation of pure bilianic acid with potassium permanganate, either alone or in acid solution; nor could Seikowski's statement be corroborated (*Monatsh.*, 17, 1) that cholic acid on oxidation with permanganate yields phthalic acid. A. W. C.

New Bile-substances. By OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1898, 24, 322—350).—The bile of the great shark (*Scymnus borealis*, Scoresby) does not yield a trace of cholesterol, and, although of a yellowish-brown colour, contains neither bilirubin nor urobilin. The mixture of sodium salts obtained by precipitating the bile acids with lead acetate, and decomposing the precipitate with sodium carbonate, although responding in a striking manner to Pettenkofer's reaction and the fluorescence test, was found to contain no glycocholic or taurocholic acid. It consisted, instead of the salts, of at least two acids containing sulphur, which differ from taurocholic acid in losing the whole of their sulphur in the form of sulphuric acid when boiled with alkalis or acids; from this they would appear to be acid ethereal sulphates, and the names α - and β -*scymnolsulphuric acid* given to them indicate their character. *Sodium α -scymnolsulphate* was precipitated from a 3 per cent. aqueous solution of the mixed sodium salts by adding an equal volume of 40 per cent. aqueous potash; it was purified by repeating this process, and was freed from potassium hydroxide by dissolving in water, nearly neutralising with sulphuric acid, saturating with carbonic anhydride, evaporating to dryness, and extracting the salt with alcohol. The pure substance is quite white, contains 5.346 per cent. of sulphur, and produces a characteristic indigo-blue coloration when dissolved in 25 per cent. hydrochloric acid; it is easily soluble in ethylic and methylic alcohols, only sparingly in acetone, and insoluble in benzene. It can be dried at 120 — 125° without decomposition, but decomposes slightly at 130° . Its aqueous solution is stable, and produces no precipitate with barium chloride; the whole of the sulphur is removed, however, as sulphuric acid when the solution is boiled with dilute hydrochloric acid. When the hydrolysis is effected by barium or potassium hydroxide, a crystalline substance, α -*scymnol*, $C_{27}H_{46}O_5$ or $C_{32}H_{54}O_6$ is produced, which melts at 100 — 101° , and is sparingly soluble in water and benzene; it easily dissolves, however, in alcohol, ether, acetone, and warm chloroform, and can be obtained in globular aggregates of needles by carefully diluting its solution in acetic acid or in alcohol. It gives Pettenkofer's reaction and the fluorescence test for cholic acid, and produces the same coloration with hydrochloric acid as sodium α -scymnolsulphate;

it resembles cholesterol in responding to Schiff's test, and that of Liebermann and Blanchard, but fails to give Salkowski's reaction.

From the composition of α -scymnol, that of sodium α -scymnolsulphate is probably $C_{32}H_{53}O_5 \cdot SO_4Na$ or $C_{27}H_{45}O_4 \cdot SO_4Na$; it was impossible to discriminate by analysis between these formulæ, since the salt could never be obtained in a sufficiently pure state; it always contained from 0.17—0.3 per cent. of nitrogen, due to an impurity. The analysis of *barium* α -scymnolsulphate, which, on adding ether to the alcoholic solution, separates as a white powder readily soluble in water, gave numbers agreeing with either of the formulæ $(C_{27}H_{45}O_4 \cdot SO_4)_2Ba + 4EtOH$ or $(C_{32}H_{53}O_5 \cdot SO_4)_2Ba$, but owing to lack of material, it was impossible to decide between them.

On hydrolysing sodium α -scymnolsulphate with hydrochloric acid, a resinous product is obtained which possibly consists of a mixture of two *dyslysins*, having the formulæ $C_{27}H_{44}O_4$ and $C_{27}H_{42}O_3$, if that of α -scymnol be assumed to be $C_{27}H_{46}O_5$.

Sodium β -scymnolsulphate was not separated in a pure state from the α -salt, which it closely resembles; it differs from the latter in being more soluble in 20 per cent. potash, and in giving a green coloration when dissolved in 25 per cent. hydrochloric acid. There appears also to be present, in very small quantity, in the crude mixture of α - and β -salts, a third substance, a γ -salt, which differs from them in producing a precipitate with copper sulphate, lead acetate, and barium chloride, and in yielding an *acid* which is sparingly soluble in water; the γ -salt, like the α - and β -salts, contains no nitrogen, and gives the Pettenkofer reaction.

When the crude mixture of α - and β -salts is hydrolysed with potash, there is produced, in addition to α -scymnol, an amorphous substance, β -scymnol, $C_{29}H_{50}O_5$, which is probably its next higher homologue; it produces the same coloration with 25 per cent. hydrochloric acid as sodium β -scymnolsulphate, and like the latter gives Pettenkofer's reaction.

W. A. D.

Urobilin. By JOHN L. W. THUDICHUM (*Virchow's Archiv.*, 1898, 153, 154—158).—This paper is largely polemical in relation to the work of Garrod and Hopkins. What they call urobilin is regarded as the omicholin previously described by the author.

W. D. H.

Urocaninic Acid. By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1898, 24, 399—409).—A crystalline sediment from the urine of a dog was found to consist of urocaninic acid (compare Jaffé, *Abstr.*, 1875, 478 and 1187); the author confirms Jaffé's formula, $C_{12}H_{12}N_4O_4 + 4H_2O$, for the latter, and points out that it does not melt sharply at $212-213^\circ$, but indefinitely at a somewhat higher temperature, which depends on the rapidity of the heating. One hundred c.c. of water dissolves, at 17.4° , 0.15 gram; at 18.7° , 0.16 gram; at 50° , 0.77 gram; and at 63° , 0.96 gram of anhydrous urocaninic acid. *Barium urocaninate*, $C_{12}H_{10}N_4O_4Ba + 2H_2O$, crystallises from water in tufts of slender needles.

No well-defined decomposition products could be obtained by acting on urocaninic acid with either oxidising or hydrolytic agents; in many

cases, no action at all took place. Bromine acts additively on urocaninic acid dissolved in acetic acid, a *dibromide*, $C_{12}H_{12}N_4O_4Br_2$, being formed, which, when dissolved in water or alcohol, decomposes into hydrogen bromide, urocaninic acid, and the product, $C_7H_6Br_4N_2O_4$, described below.

On passing bromine vapours into urocaninic acid suspended in water until the colour of the bromine ceases to be discharged, carbonic anhydride is evolved, and ammonium bromide formed, together with two distinct decomposition products. The first of these, *bromurocanidine*, $C_7H_5N_4Br_5$, is insoluble in water, ether, chloroform, benzene, and light petroleum, but easily soluble in methylic or ethylic alcohols, acetic acid, and ethylic acetate; when heated, it softens at 125° , and melts at 133° ; on reduction with zinc dust and acetic acid, it yields a crystalline substance which contains no bromine. The second decomposition product of urocaninic acid, $C_7H_5Br_4N_2O_4$, crystallises from ether in four-sided prisms, is easily soluble in water and alcohol, but insoluble in chloroform, benzene, and light petroleum.

Jaffé's formula, $C_{11}H_{10}N_4O_4H_2PtCl_6$, for the platinumchloride of urocanine is confirmed; since urocanine gives the reactions of a xanthine derivative, and produces the same physiological effects as heteroxanthine and paraxanthine, it must be classed among the purine derivatives.

No urocaninic acid could be detected in human urine, either normal or arthritic. W. A. D.

Lysuric Acid and its Salts. By CLARA WILLDENOW (*Zeit. physiol. Chem.*, 1898, **25**, 523—550).—Lysuric acid, prepared from the pure barium salt, crystallises from dilute alcohol and melts at 144 — 145° (compare Abstr., 1896, i, 268). The acid barium salt, $2(C_6H_{12}Bz_2N_2O_2) + (C_6H_{11}Bz_2N_2O_2)_2Ba + 2H_2O$, crystallises in beautiful needles and melts at 144 — 148° , at which temperature it loses its H_2O . The normal barium salt, $(C_{20}H_{21}N_2O_4)_2Ba + 1\frac{1}{2}H_2O$, is a white, crystalline powder melting at 168° . The acid sodium salt is a white, crystalline mass melting at 108 — 109° , and contains $1H_2O$. The acid strontium salt crystallises in plates, melts at 137 — 138° , and contains $2H_2O$. The normal strontium salt is crystalline, and contains $1H_2O$. The silver salt, $C_{20}H_{21}N_2O_4Ag + \frac{1}{2}H_2O$, is a white, amorphous precipitate. A. W. C.

Chemical Nature of Diastase; Determination of its Activity by the Use of Soluble Starch; and the Occurrence of an Araban in Ordinary Diastase. By AUGUSTIN WRÓBLEWSKI (*Zeit. physiol. Chem.*, 1898, **24**, 173—223. Compare this vol., i, 500, and Osborne, this vol., i, 286).—The author deals at length with work which he has already briefly summarised (this vol., i, 54). In addition, a convenient apparatus is described for dialysing diastatic preparations in a continuous stream of water; and the following method is given for preparing soluble starch. Rice-starch (100 grams) is triturated with a small quantity of 2 per cent. caustic potash, left for 2—4 hours, and then diluted to 600—800 c.c. with the 2 per cent. alkali; the product is heated, first on the water bath until the liquid is quite thin, and subsequently over a bare flame for 30 minutes, and is then

slightly acidified with acetic acid ; after precipitating with 95 per cent. alcohol, the product is twice redissolved and reprecipitated, and finally well washed with alcohol and ether. Soluble starch prepared in this way is a very white powder, which completely dissolves in water, but is insoluble in alcohol of greater concentration than 40 per cent. ; it is entirely without action on Fehling's solution. With a mixture of copper sulphate and caustic soda, it gives the same reaction as Landwehr has stated to be characteristic of animal gum. A solution of soluble starch cannot be dialysed ; it is precipitated by sodium, ammonium, and magnesium sulphate, and by tannin ; in the latter case, however, on washing the precipitate with alcohol, the tannin is removed, and the residue becomes soluble in water. Soluble starch is not precipitated by phosphomolybdic or phosphotungstic acid, potassium mercury iodide, lead acetate either normal or basic, or mercuric chloride or nitrate. Soluble starch identical with the above can be prepared by heating rice-starch for 30 minutes with water to which 2 drops of 10 per cent. caustic potash has been added ; if 10 drops of the alkali be employed, and the mixture heated during $4\frac{1}{2}$ hours, a product will be obtained which shows a slight cupric-reducing power.

By heating cane-sugar and inulin with very dilute alkalis, the author has brought about their partial hydrolysis ; this explains the fact that pure inulin reduces Fehling's solution slightly after long heating. It appears, however, that hydrolysis by alkalis, which may be considered due to free OH-ions, is far slower than that due to acids, in which hydrogen-ions play part.

The following is the author's method of estimating diastatic activity. Two grams of soluble starch is dissolved in 100 c.c. of water ; 0.01 gram of the diastase, dried at 60°, is dissolved in 10 c.c. of water, and left in contact at 40° during 8 hours, with 50 c.c. of the starch solution ; at the end of this period, the solution is boiled to destroy the diastase, and the maltose formed estimated by Fehling's solution, using Allihn's method.

The paper concludes with a critical examination of the diastases prepared by other investigators, and a valuable bibliography is appended.
W. A. D.

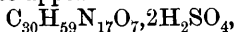
Constitution of the Simplest Proteids. By ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1898, 25, 165—189).—As, according to the earlier experiments of the author, the molecule of the complicated proteids contains an atom-complex similar to the protamine group, the more accurate chemical knowledge of the protamines should give an insight into the constitution of the albumin molecule. The author has therefore submitted the three protamines, sturine from the spermatozoa of the sturgeon, salmine from the salmon, and clupeine from herring sperm, to a closer investigation.

The protamine sulphates were prepared according to previous directions (*Zeit. physiol. Chem.*, 1895, 22, 176) and freed from the last traces of nucleic acid by precipitating an aqueous solution with sodium picrate, dissolving the precipitate in excess of sulphuric acid, and shaking the solution with ether, to get rid of picric acid ; the addition of alcohol to the evaporated solution causes the separation of the protamine sulphate.

Clupeine, $C_{30}H_{57}N_{17}O_6$.—The numerical results of the analysis of clupeine sulphate previously dried at $110-120^\circ$ agree with the formula $C_{30}H_{57}N_{17}O_6 \cdot 2H_2SO_4$. In the dry state, it is a white powder, easily soluble in warm water; on cooling the solution, a colourless, highly refractive oil is deposited, which dries on exposure to the air. Both this oil and clupeine sulphate are strongly laevorotatory.

Clupeine itself has a strongly alkaline reaction, gives a blue-violet biuret reaction, but no reaction with Millon's reagent or acetic and sulphuric acids. It is precipitated from neutral or faintly alkaline solution by potassium phosphomolybdate, molybdate, picrate, chromate or ferrocyanide, thus differing from peptones and propeptones (albumoses). Potassium tri-iodide, salts of the heavy metals, such as mercuric chloride, also bromine water, cause precipitation, the latter with formation of an unstable additive product. Clupeine, like other protamines, gives in ammoniacal solution a precipitate with coagulable albumin and albumoses.

Salmine.—The sulphate appears to have the formula



or, in other words, only differs from clupeine sulphate in containing one more molecule of water. The author inclines to the belief that this arises from the different methods of drying the substances, and that in reality salmine and clupeine are identical; a supposition supported by the facts that the two substances have the same solubility in water, and the same optical activity and refractive index.

Sturine resembles salmine and clupeine markedly in properties, but is more easily soluble. The *sulphate* is precipitated from its solutions, on adding a few drops of ether, alcohol, or acetone, as an oil probably of the formula $4C_{36}H_{69}N_{19}O_7 + 11H_2SO_4$.

When the protamines are heated with dilute sulphuric acid, *protones* or peptones of the protamines are first obtained; these resemble the protamines in their properties, but their sulphates are more readily soluble, and they give none of the characteristic precipitates of the protamines.

By the further hydrolysis of the protamines the hexon bases, histidine, arginine, and lysine, are produced, the name hexon being retained for nitrogenous substances, and obtained by the decomposition of proteids containing six atoms of carbon.

In order to separate histidine from arginine and lysine, use is made of the fact that histidine carbonate, in absence of neutral alkali salts, is precipitated by mercuric chloride, whilst the carbonates of arginine and lysine are not. Arginine, when treated with silver nitrate, gives a basic substance containing silver, and as this is precipitated by alkali, it may thus be separated from lysine.

By the use of these methods, it becomes easy to prepare crystalline specimens of these hexon bases from the protamines, the exact details of which are given in the paper. Quantitative experiments show that, under these conditions, clupeine gives 1 molecule of histidine and lysine and 3 molecules of arginine, whereas sturine gives 1 molecule of histidine, 2 molecules of lysine, and 3 molecules of arginine.

As both protamines and proteids yield histidine, arginine, and lysine under certain conditions, it seems reasonable to suppose that the albumin molecule contains a protamine complex which yields these hexon bases on treatment with acids. To this complex are attached other groups which, on decomposition, yield the amido-acids of the fatty series, a third group gives tyrosine, and a fourth group gives the decomposition products containing sulphur.

A. W. C.

Compounds of Proteids with Hydrochloric Acid, Sodium Hydroxide, and Sodium Chloride. By STEFAN BUGARSZKY and LEO LIEBERMANN (*Pflüger's Archiv.*, 1898, 72, 51—74).—Whether acids, alkalis, and normal salts form actual compounds with albumin and similar substances, has long been a moot point with chemico-physiological workers. To solve the question, two methods hitherto not used for the purpose were tried; the first consisted in a measurement of the electromotive force of the supposed compounds; the second was the cryoscopic method of observing whether any lowering of the freezing point occurs. The conclusions arrived at by both methods are the same, namely, that hydrochloric acid is really chemically united to proteid substances (albumin, albumose, pepsin); that sodium hydroxide is also united to albumose and albumin, but that sodium chloride is not.

W. D. H.

Behaviour of the Sulphur in Albumin free from Ash as Compared with that of Sulphur in the Halogen Derivatives of Albumin. By ERICH HARNACK (*Ber.*, 1898, 31, 1938—1943. Compare Abstr., 1892, 645).—Although the conversion of egg-albumin into albumin free from ash by the author's method involves no loss of sulphur, this element is not in the same condition of oxidation in both compounds; whilst ordinary albumin rapidly blackens an alkaline solution of lead oxide, this agent is without influence on the ash-free albumin. Whether the oxidation undergone by sulphur in the conversion of egg-albumin into ash-free albumin is due to atmospheric oxygen or to the copper oxide, is at present undecided, but the author does not admit the general truth of Werigo's conclusion that metallic albuminates no longer contain unchanged albumin, because lead albuminate rapidly blackens a hot, alkaline solution of lead oxide; copper, zinc, and platinum albuminates, on the other hand, do not blacken lead oxide.

Although the proportion of sulphur in albumin is not altered by the introduction of halogens, the derivatives thus obtained do not blacken an alkaline solution of lead oxide (compare Hopkins and Pinkus, this vol., ii, 503). More vigorous action of halogens appears to eliminate groups containing sulphur in three stages, and the author concludes from this result that the molecule of albumin contains three atoms of sulphur, the minimum molecular weight being nearly 5,000; it remains questionable, however, whether it will not become necessary to multiply this number by two or three.

M. O. F.

Effect of Minute Quantities of Acid on the Solubility of Globulin in Salt Solutions. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1897, 19, 482—487).—It has been previously shown (Abstr., 1893, i, 380) that the principal globulin of

the seed of the castor-oil bean is partly insoluble in a saturated solution of sodium chloride and partly soluble therein, and that these two parts are alike in composition and differ but slightly in their reactions. More elaborate experiments have been made which confirm the above statement.

Experiments were also made by adding minute quantities of acetic acid (for example, 20 c.c. of 0.05 per cent. acetic acid) to the globulin and then dissolving by adding sodium chloride (2 grams); such a solution, when diluted with twice its volume of water, gave an abundant precipitate. A similar precipitate was obtained by saturating with sodium chloride. Similar solutions without the acetic acid gave no precipitates either on dilution or on saturation. The amount of acetic acid in all cases was so minute that the solutions gave a neutral reaction with litmus paper. In this manner, it has been shown that a quantity of acid too small to be detected with litmus or by analysis causes changes in the fractions soluble in saturated salt solution. Experiments have also been made with crystallised edestin from hemp seed, and similar results have been obtained. These changes are similar to those occurring naturally in the seeds and extracts of the castor-oil bean and sunflower, but whether such changes occur only through the influence of small quantities of acid is a point not yet settled. It has been found that edestin originally soluble in 10 per cent. sodium chloride solution, after keeping in stoppered bottles for from two to four years, becomes largely insoluble, and that its solutions are precipitated by saturating with salt. J. J. S.

Iodospongine, an Iodised Proteid Present in Ordinary Sponge. By ERICH HARNACK (*Zeit. physiol. Chem.*, 1898, 24, 412—425).—The sponge employed by the author, after being cut into small pieces and extracted with dilute hydrochloric acid, contained only 0.35 per cent. of ash, and had an average composition.

C.	H.	N.	S.	I.	O.
48.51	6.30	14.79	0.73	1.50	about 28 per cent.

When left with dilute sulphuric acid (sp. gr. = 1.29) for 8 days, most of the sponge material dissolved and a powdery substance separated; this was twice dissolved in dilute caustic soda, and twice precipitated with dilute sulphuric acid, and purified for analysis by dissolving in ammonia, precipitating with ammonium sulphate, and dialysing the product. The substance thus obtained has the composition $C_{56}H_{87}IN_{10}S_3O_{23}$; if in its preparation the sulphuric acid is replaced by hydrochloric acid, a product containing less sulphur is formed; this probably has the composition $C_{56}H_{87}IN_{10}S_2O_{20}$, although a complete analysis was not made, owing to the difficulty of its preparation. To the latter substance, the name *iodospongine* is given, the former probably being its *monosulphonic acid*. This when freshly prepared is colourless, but soon darkens to a brownish-black; it dissolves in alkalis, but is reprecipitated by acids or ammonium sulphate; it produces a black coloration with alkaline lead oxide, but fails to give the biuret test, the sugar reaction in presence of α -naphthol (Molisch), or Adamkiewicz's reaction.

Since the ratio of sulphur to iodine is the same in iodospongine as

in the original sponge material (2 atoms of sulphur to 1 atom of iodine), the author concludes that a portion of the molecule of the latter has been split off which contains the whole of the iodine and sulphur; this portion is almost exactly one-sixth of the weight of the total molecule.

W. A. D.

Formation of Arginine from Elastin. By ALBRECHT KOSSEL and FR. KUTSCHER (*Zeit. physiol. Chem.*, 1898, 25, 551—552).—Bergh and Hedin (this vol., i, 608) have recently stated that Kossel's hexon bases are not obtainable from elastin, and that therefore a new group of proteid-like substances must be provided in Kossel's new scheme of classification. In the present research, it is shown that elastin from the *ligamentum nuchæ* does yield a small amount of arginine (0.3 per cent.). This is the easiest of the hexon bases to prepare. There is, therefore, no reason to doubt that elastin contains a protamine nucleus.

W. D. H.

Formation of Levulinic Acid from Nucleic Acid. By ALFRED NOLL (*Zeit. physiol. Chem.*, 1898, 25, 430—433).—The nuclein of yeast and of pancreas yields a reducing carbohydrate. Such a substance, however, is not obtainable from nucleic acid, although Kossel and Neumann showed that by the action of sulphuric acid at a high temperature on the nucleic acid of the thymus, levulinic acid (with formic acid) is obtainable; this appears to indicate the existence in nucleic acid of a carbohydrate complex. In the present research, nucleic acid was prepared from the spermatozoa of the sturgeon, and Kossel's result was confirmed.

W. D. H.

Mucin from an Ovarian Cyst. By CHARLES LEPIERRE (*Compt. rend.*, 1898, 126, 1661—1664).—The gelatinous contents of an ovarian cyst, when boiled with water, filtered, and the filtrate acidified with acetic acid, yielded 4 per cent. of a *mucin* differing in some particulars from those hitherto described, and having the percentage composition: carbon, 49.2; hydrogen, 7.0; nitrogen, 12.6; sulphur, 0.94; mineral matter, 0.5; undetermined, 29.76. These figures show that the substance is allied to the mucins obtained from the submaxillary glands and from tendons. It is not affected by dilute alkalis (1:1000), but on warming with more concentrated solutions of potash or soda, a clear yellow solution is obtained which, on adding acetic acid, yields either no precipitate or else one which is dissolved by excess of the acid. It is not dissolved by dilute acids in the cold, but on heating it is hydrolysed into albumoses and a *carbohydrate* of the formula $C_6H_{12}O_6$. The latter, which is inactive and non-fermentible, readily reduces Fehling's solution, and forms an *osazone* crystallising in yellow needles, and melting at 164—165°. The aqueous solution of the mucin is not coagulated by heat, nor does it reduce Fehling's solution; it is precipitated by neutral salts, tannin, mercuric chloride, &c., but in no case is the precipitate dissolved by excess of the reagent. When treated with pepsin and dilute hydrochloric acid at 45°, the mucin is converted into a mixture of mucin-albumose and mucin-peptone, which may be separated by means of ammonium sulphate.

N. L.

The Proteid of Hæmoglobin. By FRIEDRICH N. SCHULZ (*Zeit. physiol. Chem.*, 1898, **24**, 449—481).—Pure crystalline oxyhæmoglobin is conveniently prepared from horse's blood by adding sufficient ammonium oxalate to prevent coagulation, allowing the corpuscles to subside, and diluting the latter with twice their volume of water; on adding to the solution an equal volume of saturated ammonium sulphate, and cooling to 0°, the fibrinogen and globulin are precipitated, whilst the oxyhæmoglobin remains dissolved; the solution is filtered at 0°, and left to stand until the whole of the oxyhæmoglobin has separated. Thus prepared, the latter is perfectly free from methæmoglobin, and can be kept some time without change.

When a very small quantity of dilute hydrochloric acid is added to a solution of hæmoglobin, a brown precipitate is formed, which immediately dissolves in an excess of acid; on now adding alcohol ($\frac{1}{5}$ vol.), and shaking with ether, the whole of the colouring substance is removed by the latter, whilst a yellowish precipitate is thrown down from the alcoholic solution on the addition of ammonia. On dissolving this in very dilute acetic acid, precipitating with ammonia, filtering, and washing with absolute alcohol and ether, nearly pure *globin* is obtained. This contains C=54·97, H=7·20, N=16·89, S=0·42 per cent., and must be distinguished from Preyer's "globin" obtained from methæmoglobin. Its aqueous solution is not coagulated by heat; on adding a trace of ammonia, caustic soda, or sodium carbonate, a flocculent precipitate is produced, which dissolves in the slightest excess of the alkali; if, however, the aqueous solution of globin is acidified with hydrochloric acid, an excess of ammonia produces a permanent precipitate.

Globin gives the biuret, xanthoprotein, Millon's, and Adamkiewicz's reactions; like the acid albumins, it dissolves in dilute acids, and is precipitated unchanged on exactly neutralising the latter; it differs however, from them in not being coagulable by heat, and in the behaviour of its aqueous solutions towards small quantities of nitric and hydrochloric acids; these produce coagula which dissolve when the solutions are warmed, and are reprecipitated on cooling. This behaviour resembles that of the primary albumoses, although globin differs from these in being insoluble in dilute solutions of sodium chloride and ammonium sulphate. Globin is in its properties most closely allied to the histons of Kossel (*Abstr.*, 1885, 572), and of Lilienfeld (*Abstr.*, 1894, ii, 146); these, however, contain on the average 52·26 per cent. of carbon, 7·19 per cent. of hydrogen, and 18·46 per cent. of nitrogen, and have therefore a very different composition from globin. It is also noteworthy that, whereas Lilienfeld's histon, when intravenously injected, is capable of preventing the coagulation of blood subsequently withdrawn, globin exercises no such influence under similar conditions. When large quantities of globin are injected, the latter is found in marked quantity in the urine; in the author's opinion, the presence of histon in the urine (compare Kolisch and Burián, *Abstr.*, 1897, ii, 112) can equally well be attributed to the red blood corpuscles as to the leucocytes.

The author's analyses of horse's hæmoglobin give C=54·56; H=7·15; N=17·33; and S=0·43 per cent.; these values agree closely with

those of Hoppe-Seyler and of Otto and Bücheler. It would seem that hæmatin and globin are not the sole products of the decomposition of hæmoglobin; a substance having the reactions of a primary albumose appears to be formed in small amount.

The globin obtained from the hæmoglobin of dog's blood appears to be identical with that from horse's hæmoglobin; the blood of the goose, however, yields a globin which possesses different properties, and is possibly a nucleohiston.

W. A. D.

Hæmochromogen. By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1898, 25, 492—506).—Hæmochromogen was prepared by reducing an ammoniacal alcoholic solution of hæmatin with hydrazine hydrate in an apparatus from which both oxygen and moisture could be excluded; it is precipitated from solution by a mixture of alcohol and ether, as a red, amorphous substance, resembling red phosphorus in appearance. The following numbers are the mean of five analyses of this preparation: C=63·83; H=5·66; Fe=9·25; N=11·48; and O=9·78. Unfortunately, as the formula of hæmatin is doubtful, these results cannot lead to any definite conclusion regarding the constitution of hæmochromogen.

When an ammoniacal solution of hæmochromogen is neutralised with acetic acid, a voluminous, brownish-red precipitate is obtained, which contains iron, and on redissolving in ammonium hydroxide, shows the characteristic spectrum of hæmochromogen.

Hæmochromogen appears to be the only product of the action of hydrazine hydrate on hæmatin; with oxyhæmoglobin and methæmoglobin the reaction goes further. As shown by the spectroscope, hæmoglobin is first formed in both cases, then hæmochromogen, and after a time the solution becomes completely decolorised. Curves are given comparing the extinction coefficients of a 0·0082 per cent. ammoniacal solution of hæmochromogen with a solution of hæmatin of like strength.

A. W. C.

JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Molecular Refraction and Dispersion of very Dilute Solutions. By D. DIJKEN (*Zeit. physikal. Chem.*, 1897, **24**, 81—113).—The refractive indices of a number of dilute salt solutions were determined, and the molecular refraction of the dissolved salt calculated by means of Gladstone's expression; this value is found to be a constitutive property, as is shown in the appended table.

	Cl.	NO ₃ .	$\frac{1}{2}$ SO ₄ .
NH ₄ — $\frac{1}{2}$ Mg.....	7·7	7·8	7·8
NH ₄ — $\frac{1}{2}$ Zn.....	6·8	6·0	6·0
NH ₄ —Li.....	7·8	7·1	7·7
NH ₄ —Na.....	6·7	6·9	6·7
NH ₄ —K.....	3·4	3·6	3·4
NH ₄ —H.....	8·0	8·2	8·4
K—Na.....	3·3	3·3	3·3

The molecular refraction of ammonium chloride is 22·5, of the nitrate 25·8, and of the sulphate ($\frac{1}{2}$ SO₄) 19·9, and from these values those of the other salts can be readily obtained. L. M. J.

Red Spectrum of Argon. By JOSEF MARIA EDER and EDUARD VALENTA (*Monatsh.*, 1895, **16**, 893—895).—By means of a concave grating, the spectrum of argon at a pressure of 1—3 mm. was obtained,

and the wave-lengths of the lines measured reduced to Rowland's scale. Both the red and blue spectra were obtained, and a table of the wave-lengths of the lines of the red spectrum from 5060 to 3319 is given. The following are given as specially characteristic: $\lambda = 4628\cdot56$, $4596\cdot22$, $4522\cdot49$, $4510\cdot85$, $4300\cdot18$, $4272\cdot27$, $4259\cdot42$, $4251\cdot25$; the group $4200\cdot76$, $4198\cdot42$, $4182\cdot07$, $4164\cdot36$, and $4158\cdot63$; and further, $4044\cdot56$, $3949\cdot13$, $3834\cdot83$. When the dispersion is good, the double line $4191\cdot15-4190\cdot75$ should show up plainly in the red spectrum of argon.

H. C.

Chemistry of the Hottest Stars. By Sir J. NORMAN LOCKYER. (*Proc. Roy. Soc.*, 1897, **61**, 148—208, and 213).—The author summarises his own investigations and those of others on the spectra of metals at high temperatures and on stellar spectra, and arrives at the following general conclusions.

In a mixture of vapours at a particular temperature, a vapour which is not present in sufficient quantity to show all the lines of its spectrum will be represented by the lines which are longest in its spectrum at the particular temperature in question. Only some of the short lines in metallic spectra represent the effects of high temperature. Some of the substances which have been investigated, including iron, calcium, and magnesium, have probably a definite spectrum, consisting of a few lines, which can only be completely produced at a temperature higher than any which is at present available in laboratory experiments. The lines constituting the new spectra are those which either appear only in the spark spectrum, or are lengthened in passing from the arc to the spark; such lines are termed enhanced lines. In the case of iron, calcium, and magnesium, there are four distinct temperature steps which are marked by spectral changes: (*a*) The flame spectrum, (*b*) the arc spectrum, (*c*) the spark spectrum, (*d*) a spectrum consisting solely of those lines which are enhanced in passing from the arc to the spark.

The order of temperature of certain stars, as determined from a comparison of the extensions of the continuous spectrum into the violet or ultra-violet, is precisely the same as that which follows from a comparison of the metallic spectra at the four stages of temperature. The variations of the metallic lines furnish the most convenient means of determining relative stellar temperatures, for the reason that photographs with special exposures are unnecessary. Having ascertained the relative temperature of a star in this way, and assuming that all the absorbing vapours are at the same temperature, the presence or absence of any other metallic substance can be determined by looking for the lines which are longest in its spectrum at that temperature. In the case of the hottest stars, the fourth stage spectrum must be the term of comparison.

Accepting the new results with regard to the lines enhanced in the spark, several lines in the spectra of the hottest stars, for which no origins could previously be assigned, can now be ascribed to metallic substances at the fourth stage of temperature. The lines of the cleveite gases appear only in the hotter stars, as indicated by the extension of the continuous radiation into the ultra-violet, and they increase in intensity

with increased temperature in certain stars. The order of stellar temperatures, determined from the *increasing* intensity of the lines of the cleveite gases, is identical with that determined from the *decreasing* intensity of the metallic lines in the case of those stars which show both series of lines.

Different substances are spectroscopically visible through different ranges of stellar temperatures. The hydrogen lines are visible in stars ranging in temperature from that of α -Orionis to that of Bellatrix, whilst those of the cleveite gases do not appear below the temperature of α -Cygni. The enhanced lines of calcium appear at temperatures as low as α -Orionis, and persist, with reduced intensity, to the temperature of Bellatrix; those of iron do not appear at temperatures lower than that of α -Cygni, and disappear altogether at the temperature of Bellatrix; while the enhanced line of magnesium appears at the temperature of α -Cygni, and remains feebly visible at the temperature of Bellatrix. It follows, then, that the enhanced metallic lines may be absent from a stellar spectrum, either because the temperature is too low or too high.

In the case of those stars which previous investigations have shown to be cooling, the metallic line phenomena are inverted. The enhanced lines first become visible, then the arc lines; but whereas the enhanced lines disappear at a certain stage in the process of cooling, the arc lines continue to become stronger. The lines of the cleveite gases show a similar inversion on the downward side of the temperature curve; strongly represented in the hottest stars, they thin out very rapidly in cooling stars, and disappear before the arc lines have begun to show themselves.

Utilising the iron lines as a method of bringing together stars of approximately equal temperature, it is found that at each stage the stars are divisible into two groups, which, in accordance with the author's previous work, correspond with increasing and decreasing temperatures respectively. As determined in this way, stars of increasing temperature differ from those of decreasing temperature at the same stage of heat: (1) in the greater continuous absorption in the violet or ultra-violet; (2) in the generally greater intensity and breadth of the metallic lines; (3) in the smaller thickness of the hydrogen lines; (4) in the greater thickness of the helium lines at those stages at which they are visible. These differences are all explained on the meteoritic hypothesis. There are stars, near and at the top of the curve, which cannot be arranged in order of temperature by the criteria referred to, for the reason that the iron lines have disappeared, and the lines of hydrogen and cleveite gases show little variation. The arrangement of stars about the top of the curve will depend on the conditioning of certain lines, at present of unknown origin; the necessary criteria, therefore, require further investigation.

The known facts with regard to changes in the line spectrum of an element can be easily explained on the hypothesis of successive dissociations analogous to those observed in the case of undoubted compounds. Similarly, the differences in the lines representative of a metal such as iron in the spectra of sun-spots, prominences, chromosphere, or different stars, are explained by supposing that there are

different molecular groupings at each stage of temperature. The change from a continuous spectrum to one consisting of flutings, and afterwards to one of lines, is now acknowledged to be due to the existence of different molecular combinations. The recent investigations of Humphreys and Möhler on the shifts produced in metallic lines, confirm the author's view that the line spectrum of a metal integrates for us the vibrations of several sets of molecules. It is argued that the existence of "series" of lines in the spectra of some chemical elements is another indication of molecular complexity, each series probably representing the vibrations of similar molecules. The behaviour of the magnesium lines in stellar spectra is ascribed by Schreiner to differences of temperature, in accordance with the author's experimental results of 1879. The experiments on the spectrum of mercury which have been made by Eder and Valenta (*Abstr.*, 1896, ii, 2) have revealed variations which, according to them, favour the dissociation hypothesis.

On various grounds, the view that the differences in stellar spectra represent fundamental differences of chemical composition is untenable; the fact that many stars that are widely separated in space give identical spectra, indicates that they not only contain the same "elements," but that the "elements" exist in the same proportions in all. On the non-dissociation hypothesis, the action of heat on the sun's chromosphere could not produce such a spectrum as that which we know to be associated with hotter stars, since the relative proportions of different vapours could not be changed; the only change which can be imagined to take place on this hypothesis, is a reduction of intensity of all the lines due to reduced pressure.

On the dissociation hypothesis, increased temperature would bring about fundamental changes in the spectrum, due to molecular simplifications, and in this way the effect of an increase of temperature on the sun's chromosphere, as indicated by hotter stars, can be predicted, and receives a simple and sufficient explanation. The disappearance of the enhanced iron lines in the hottest stars, and the simultaneous intensification of the lines of hydrogen, helium, and an unknown gas X, bring us face to face with the fact that iron is a compound into the ultimate formation of which one or all of these gases enter. The ultimate molecules of the chemical elements discussed in this paper are arranged by the author in the following order of resistance to the effects of temperature: Gas X, helium, hydrogen, calcium, magnesium, iron.

The author concludes by claiming that laboratory, solar, and stellar evidence has more and more demonstrated the truth of the dissociation hypothesis, and that we can now acknowledge that the phenomena of the inorganic world are dominated by an evolution not less majestic, although much more simple, than that now universally accepted in the case of organic nature.

H. C.

Chemical Constitution of the Stars. By ARTHUR SCHUSTER (*Proc. Roy. Soc.*, 1897, 61, 209—213).—While agreeing with Lockyer's general statement (see preceding abstract) that the chemical elements in the stars are the same as those in the sun, the author is not convinced that the difference in the spectra of stars is not due to a real

difference of constitution. Some of the stars which are now in an early stage of development may be forming through the condensation of matter which has been left over by others; and it would not be surprising if the youngest star did not agree in constitution with its aged companions. If Lockyer's dissociation hypothesis is correct, we must look forward to finding some trace of helium, or calcium, or hydrogen in the discharge taken from iron poles. Not till then will this hypothesis be considered as proved. H. C.

Two New Galvanic Cells. By H. PAULING (*Zeit. Elektrochem.*, 1897, 3, 332—333).—The first cell described has carbon electrodes immersed respectively in concentrated chlorine water and sodium thiosulphate solution, the liquids being separated by a porous pot soaked in brine. The electromotive force fell, on short circuit, from 0.64 volt to 0.47 volt and then remained constant for 5 hours, the current passing being 0.7 amp. Sulphur separates out in the thiosulphate solution.

In the second cell, the electrodes are iron and carbon respectively, and the electrolyte a concentrated solution of ferric chloride, the reactions which take place, according to the author, being $3\text{FeCl}_3 = 3\text{FeCl}_2 + 3\text{Cl}$ and $\text{Fe} + 3\text{Cl} = \text{FeCl}_3$. The ferrous chloride formed is reconverted into ferric chloride by means of chlorine gas. The electromotive force of the cell is 0.9 volt and its principal advantages are its freedom from smell and cheapness. A simple mode of construction is described in which a constant flow of ferric chloride solution is maintained through the cell so as to ensure efficient depolarisation. T. E.

The Iron-Carbon-Ferric Chloride Cell. By FRIEDRICH W. KÜSTER (*Zeit. Elektrochem.*, 1897, 3, 383—385).—The process occurring in the cell described by Pauling (see preceding abstract) is better represented by the equation $2\text{Fe}''' + \text{Fe} = 3\text{Fe}''$, the dashes indicating the number of positive charges of electricity.

Since the iron is always contaminated with finely divided carbon or iron carbide, local galvanic action must occur of the same kind as the main reaction taking place in the cell. That this is the case was proved by an experiment in which the iron plate lost 1.66 grams in weight, whereas the loss corresponding to the quantity of electricity produced should have been 0.31 gram.

That the iron dissolves as ferrous chloride and not as ferric salt was shown by immersing the iron plate in a solution of sodium chloride and the carbon plate in a solution of ferric chloride. After allowing the current to pass for some time, the solution in the vicinity of the iron plate was found to contain ferrous salt alone without a trace of ferric iron. T. E.

Determination of the Resistance of Galvanic Cells with small Polarisation Capacity. By ERNST HAAGN (*Zeit. Elektrochem.*, 1897, 3, 470—471. See also Gordon, *ibid.*, 3, 162, 1896; and Haagn Abstr., 1897, ii, 393).—If the resistances in the arms of a Wheatstone bridge are R_1 , R_2 , R_3 , and R_4 (R_3 and R_4 referring to the halves of the bridge wire), and the arms 1 and 2 contain in addition capacities C_1 and C_2 , balance is obtained when $R_1/R_2 = R_3/R_4$ and $R_3/R_4 = C_2/C_1$ simultaneously. The present method is based on this. The cell of

which the resistance (R_1 say) is to be measured has a capacity C_1 . The measurements are made by the telephone method, and in order to get a good minimum, the arm of the bridge containing the comparison resistance R_2 must also contain a condenser of capacity C_2 fulfilling the requirements of the above equation. A suitable condenser may be made by immersing two aluminium plates in sulphuric acid of maximum conductivity; a current is then passed between them with an E. M. F. of about 10 volts for a minute, when the aluminium plates become polarised so that a smaller E. M. F. than 10 volts causes no current to pass in the same direction, and this condition is retained for a considerable period. The capacity of the condenser is varied by varying the depth to which the plates are immersed in the acid. In order to prevent direct current from the cell passing through the telephone circuit, an air condenser is included in it. The measurement is made by first adjusting the bridge contact to an approximate minimum of sound in the telephone, a nearer approximation is obtained by adjusting the depth of immersion of the aluminium plates, and then the final adjustment of the bridge contact is made. The method is applicable whether current is flowing through the cell or not.

T. E.

Theory of Accumulators. By FRITZ FOERSTER (*Zeit. Elektrochem.*, 1897, 3, 525—531).—The author discusses the rival theories of the action taking place in a lead accumulator, supported on the one hand by Le Blanc, on the other by Liebenoff and Löb (*Abstr.*, 1897, ii, 239, 300, 394). According to Le Blanc, the lead peroxide passes into solution, during the discharge, in the form of hydroxyl ions and quadrivalent lead ions, the latter then give up half their charge to the anode and are converted into bivalent lead ions. During the charging, salts of quadrivalent lead are formed at the anode which are hydrolysed, depositing lead peroxide. According to Liebenoff, solutions of lead salts contain

some PbO_2 ions which simply lose their charge at the anode, being converted into lead peroxide, the reverse change occurring during discharge. The author supports Le Blanc's view on the grounds that quadrivalent lead ions really are formed at the anode when lead salts are electrolysed [the salt $(NH_4)_2PbCl_6$ may be prepared by the electrolysis of a solution of $PbCl_2$ and NH_4Cl at 0°]. Further, according to the theory, the process of discharge is not a complete reversal of the charge, which explains the fact that the whole of the electrical energy used in charging cannot be recovered, and finally reactions in which an ion loses part of its charge are very numerous; a summary of such reactions is given. On the other hand, if Liebenoff's theory is accepted, we should expect solutions of zinc oxide or copper oxide in alkalis to deposit peroxides in the same way as a solution of lead oxide. This difficulty is avoided by assuming the formation of quadrivalent lead ions, because neither zinc nor copper is capable of forming ions of higher valency than two.

T. E.

Influence of Manganese Compounds on Lead Accumulators. By GEORG VON KNORRE (*Zeit. Elektrochem.*, 1897, 3, 362—364).—A freshly charged positive accumulator plate placed in dilute sulphuric acid containing a little manganese sulphate quickly oxidises the latter

to permanganic acid. The same result is obtained with lead peroxide although more slowly. The formation of permanganic acid is also observed when manganese peroxide is deposited in any way on the accumulator plate.

A negative accumulator plate quickly decolorises dilute sulphuric acid coloured red with permanganate. Pure spongy lead has the same effect. It follows, therefore, that manganese compounds in lead accumulators merely serve to carry oxygen from the positive to the negative plates, thereby discharging the cells. T. E.

Depolarisation of Mercury and Platinum Electrodes. By KARL R. KLEIN (*Ann. Phys. Chem.*, 1897, [ii], 62, 259—279).—The size of the polarised electrode, as long as this remains small in comparison with the other electrode, has no influence on the depolarisation. The rate of depolarisation decreases as the time occupied by the preceding polarisation increases, moreover, the rate of depolarisation increases with the temperature. The presence in the electrolyte of a salt, the metallic radicle of which is the same as the metal of the electrodes, and the acid radicle that of the electrolyte, increases the rate of depolarisation of the cathode. The rate of depolarisation of platinum electrodes is generally smaller than that of mercury electrodes in the same electrolytes. Anodic polarisation disappears at a slower rate than that of the cathode. H. C.

Temperature Coefficient of the Potential of the Calomel Electrode with various Dissolved Electrolytes. By THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1897, 24, 39—54).—The temperature coefficient of a calomel electrode in the chain $\text{Hg} \mid \text{HgCl} \mid \text{MCl} \mid \text{HgCl} \mid \text{Hg}$ was found by Gockel (*Ann. Phys. Chem.*, 1885, 24, 618), to vary considerably with the salt employed, a result at variance with theoretical deductions. The author therefore repeated Gockel's experiment, employing solutions of various chlorides at various concentrations. In the case of hydrogen chloride, the temperature coefficient was found to increase rapidly with the dilution, and the presence of small quantities of impurities was shown to have but little effect, the coefficient, moreover, decreasing with rise of temperature. The variations were found to be due to the formation of mercuric salts, $\text{Hg}_2\text{Cl}_2 = \text{HgCl}_2 + \text{Hg}$, and this reaction is largely dependent on the concentration of the dissolved chloride, but is only slightly affected by its nature. With N/10 and N/100 solutions, the effect is comparatively unimportant, and for these the observed values for the temperature coefficient are compared with those calculated by aid of a formula derived from Nernst's expression $\pi = RT/\epsilon_0 \cdot \log. P/p$. The nature of the kation only affects the value by changing the degree of dissociation, and the values agree with the observed numbers very satisfactorily except in the case of hydrogen chloride and ammonium chloride, both of which behave irregularly.

(NOTE).—No reference is made to Gockel's later paper (*Ann. Phys. Chem.*, 50, 696, Abstr., 1894, ii, 78). L. M. J.

Currents with Polarizable Electrodes. By ERNST SALOMON (*Zeit. physikal. Chem.*, 1897, 24, 55—80).—In an electrolytic cell, the

current produced by small electromotive forces is given by the expression $I = (E - E')/R$ where E is the E. M. F. and E' the E. M. F., due to polarisation; the author's experiments were performed to prove that the polarisation E. M. F. may be calculated by Nernst's formula, $E_1 = 0.058 \log. (c_2/c_1)$, the ratio c_2/c_1 being calculable from the diffusion coefficients, the polarising E. M. F., and the total concentration of the ions. The experimental methods are described, diagrams of the apparatus being given together with tables of the calculated and observed values for the current strength. The first set of tables for silver salts show no agreement, and the author finds this is always the case when the solutions are quite neutral. When, however, the solutions are made slightly alkaline or acid, the values obtained agree well with the calculated numbers in the case of silver salts, but with copper and lead salts, secondary reactions render comparisons valueless. By reverse calculation, it is possible to determine the concentration of the ions from the current strength, and the author in this manner finds the solubility of silver chloride to be 81.4×10^{-7} gram-molecules per litre [118×10^{-7} Kohlrausch]. If silver electrodes are employed in a potassium chloride solution, no current passes if the E. M. F. is small; on the addition of silver nitrate, the current is very small until all the chloride has been precipitated, when it increases enormously, so that this increase may be used to indicate the end point of a titration, the author finding the indication sensitive to 1/100 c.c. in the case of a 0.7N solution. L. M. J.

Dielectric Constants of certain Frozen Electrolytes at and above the Temperature of Liquid Air. By JOHN AMBROSE FLEMING and JAMES DEWAR (*Proc. Roy. Soc.*, 1897, 61, 299—316. Compare Abstr., 1897, ii, 475).—The dielectric constants at low temperatures of a number of frozen electrolytes were determined. Frozen electrolytes at low temperatures are capable of acting as dielectrics even in the case of those substances which in the liquid state and in aqueous solutions have relatively a very high electrolytic conductivity. At temperatures not far below their freezing points, these electrolytes have dielectric constants of large value, and numerically of the order of that of ice or water at 0°, or in some cases much larger, as, for example, with 5 per cent. and 10 per cent. solutions of sodium and potassium hydroxide. The majority of these high dielectric values, so far as observed, are reduced to very much lower values (near to 3) when the dielectrics are cooled to, and below, the temperature of liquid air. Certain aqueous solutions of potassium hydroxide retain their high dielectric values to nearly the liquid air temperature, but give indications of being reduced at lower temperatures to small values. A 5 per cent. alcoholic solution of caustic potash behaves quite differently from the 5 per cent. aqueous solution, and has a much lower dielectric constant at -185° . Frozen electrolytes at very low temperatures have very great insulating power, but recover sensible conductivity with great rapidity at temperatures far below their melting points. It appears probable that at the absolute zero of temperature all electrolytes become perfect non-conductors of electricity or have infinite resistivity, and also that it is possible their dielectric constants may be all reduced to, or represented

by, a number near to 2 or 3 at that temperature, that of a vacuum being taken as unity.

H. C.

Dielectric Constants of Pure Ice, Glycerol, Nitrobenzene and Ethylenic Dibromide at and above the Temperature of Liquid Air. By JOHN AMBROSE FLEMING and JAMES DEWAR (*Proc. Roy. Soc.*, 1897, **61**, 316—330).—The dielectric constant of pure ice at the temperature of the melting point is represented by a number not far from 80, but an enormous decrease in the constant takes place in cooling from 0° to -185° , so that at -185° the value obtained is about 2.42. As the dielectric constant of water decreases when the temperature is raised above 4° , it follows that there is unquestionably some temperature at which ice-water has a maximum value for its dielectric constant. Experiments made with ice from ordinary distilled water indicate that this temperature may, and probably does, vary with the presence of slight impurities in the water, and with the frequency of the electromotive force reversals.

The dielectric constant of glycerol is found to increase rapidly with rising temperature between -185° and -52° , the resistance at the same time falling.

Ethylenic dibromide presents a remarkable contrast to water or glycerol; its dielectric constant at 15° has a value of about 5, it falls on freezing to nearly 3, and it continues nearly constant down to the lowest temperature reached, at which it becomes 2.7. When cooled down after freezing, its resistance also remains exceedingly high and constant.

In the case of nitrobenzene, the dielectric constant, on solidification at 3° , falls somewhat rapidly from the high value of 32 to a low value of between 3 and 4, and ultimately reaches 2.61 at -185° . The resistance remains practically constant and exceedingly high during the rise of temperature from -200° upwards.

From the results, it appears that water, glycerol, ethylic alcohol and many other substances have a maximum value for their dielectric constants at certain temperatures. This makes generalisations such as those of Abegg (*Abstr.*, 1897, ii, 240) who calculates the dielectric constant of water at the absolute zero as 372, very untrustworthy.

H. C.

Dielectric Properties of Liquid Mixtures, especially of Dilute Solutions. By JAMES C. PHILIP (*Zeit. physikal. Chem.*, 1897, **24**, 18—38).—The dielectric constant was determined for a number of liquid mixtures, and the values calculated by the mixture rule, both Gladstone's and Lorenz's formulæ being employed with substitution of $\sqrt{\kappa}$ for the refractive index. In the case of mixtures of benzene with ethylic ether, and of chloroform with carbon bisulphide, the observed values agree fairly well with the calculated numbers, lying generally between those obtained from the two formulæ, but with a mixture of ether and chloroform no such agreement can occur, as the constant increases to a maximum greater than that of either constituent. In all these cases, the constants of the two liquids are not far removed, but in those cases where they differ considerably, such as ethylic alcohol with chloroform, ethylic ether, carbon bisulphide, or benzene, the

calculated values, except at great dilutions, are too low, those obtained by the Lorenz formula being only about one-half the actual values, the Gladstone formula giving far better agreement and being subsequently employed. Dilute solutions were then examined, and it was found that for solutions of nitrobenzene in benzene the calculated and observed values agree fairly well, and the discrepancies are attributed to the formula. The dielectric constant of nitrobenzene, as calculated from that of the mixture, is hence approximately constant, but with solutions of alcohols in benzene and toluene this is no longer the case, the value of the dielectric constant of the alcohol falling as the dilution increases, until a final limiting value is reached, these values being respectively : methylic alcohol, 16 ; ethylic alcohol, 11 ; propylic alcohol, 8.5 ; and amylic alcohol, 6. The author considers it probable that these are the values corresponding with the simple molecules, the dielectric constants obtained from the pure liquids being those due to molecular aggregates.

L. M. J.

Electrochemical Method of changing Alternating into Direct Currents. By LEO GRAETZ (*Ann. Phys. Chem.*, 1897, [ii], 62, 323—327).—An electrolytic cell, one of the electrodes of which is composed of aluminium, causes a great decrease in the strength of any current sent through it when the aluminium electrode is the anode, and the separation of oxygen takes place on it, but leaves the current unaffected when the aluminium is the cathode. If through a series of such cells an alternating current is sent, and the number of cells is so chosen that the anode polarisation balances or is greater than the tension of the current, the positive portion of the current, for which the aluminium would act as anode, is checked and only the negative current passes. On this principle, a method of converting an alternating current into a direct current is based.

H. C.

Molecular Conductivity of Salts in Dilute Solution. By P. JOUBIN (*Compt. rend.*, 1897, 124, 228—229).—The author supports Bouty's view that the molecular conductivity of certain salts is the same for infinite dilution, by showing, in the case of potassium chloride, that the quantity of electricity which is transferred by one molecule through the solution is that which is induced by the uniform field in which it is placed.

H. C.

The Copper Voltameter. By FRITZ FOERSTER (*Zeit. Elektrochem.*, 1897, 3, 479—482 and 493—497).—The author discusses the errors of the copper voltameter and the methods of avoiding them, in the light of his previous experiments on the electrolysis of copper sulphate solutions (Foerster and Seidel, *Abstr.*, 1897, ii, 241). The use of a concentrated solution of copper sulphate is necessary in order to prevent the deposition of the copper in a powdery form ; it has the disadvantage that it increases the concentration which may be reached by the cuprous ions, but the solution never becomes saturated with the latter owing to their oxidation by the air. For this reason, the quantity of copper deposited when the solution is exposed to air is too small, especially with smaller current densities. This action of the atmospheric oxygen explains the fact that a copper plate partially immersed

in an acidified solution of copper sulphate is most strongly acted on at the surface of the liquid. The addition of sulphuric acid to the copper sulphate solution diminishes the concentration of the cuprous ions to some extent, it is of more importance, however, in preventing the separation of cuprous oxide which takes place in neutral solutions owing to the hydrolysis of cuprous sulphate. The deposition of cuprous oxide not only increases the weight of the deposit on the cathode, but produces inequalities in its conductivity which give rise to the formation of cuprous ions where the current density is smallest. Since the presence of the acid diminishes the solubility of copper sulphate, a saturated solution of the latter cannot be used, as this would lead to deposition of the salt on the anode, entailing a large increase in resistance. A suitable solution is one containing 125 grams of $\text{CuSO}_4 + 5\text{H}_2\text{O}$, and 50 grams of H_2SO_4 per litre. In presence of air, the strongly acid solution dissolves no more copper than one containing little acid. Thus a normal solution of copper sulphate, which was also normal with respect to sulphuric acid, dissolved 17 milligrams of copper, whilst a solution containing 1/1000 of an equivalent of sulphuric acid dissolved, under the same circumstances, 15 milligrams.

In order to measure very small currents, a closed voltameter is used with a solution containing 1/10 or 1/20 gram equivalent of copper sulphate, and 1 gram equivalent of sulphuric acid, a slow current of purified hydrogen being passed through the solution during the experiment. The quantity of cuprous ions which can be formed under these circumstances is very small, and their conversion into cupric ions, at the anodes, is prevented almost completely by enveloping the latter in parchment paper. By comparison with a silver voltameter, it was found that the error in the quantity of copper deposited did not exceed a fraction of a milligram, even with a current density of 0.025 ampère per sq. dm.

The maximum current density with which an adherent deposit of copper can be obtained is higher the greater the concentration of the copper sulphate and the more thoroughly it is stirred so as to avoid local dilution near the cathode. With a solution of copper sulphate and sulphuric acid, both of normal strength, 2 ampères per sq. dm. may be safely employed.

The author finally discusses the possibility of using the loss of weight of the anode as a measure of the current, and concludes that no advantage would be obtained by so doing.

T. E.

Electrolysis of Alkali Bromides and Fluorides. By HEINRICH PAULI (*Zeit. Elektrochem.*, 1897, 3, 474—478).—The author has extended Oettel's work (*Abstr.*, 1896, ii, 517) on the electrolysis of aqueous solutions of chlorides to solutions of potassium bromide; the results are very similar to those obtained with potassium chloride, except that the yield of potassium bromate is less than that of chlorate under the same circumstances, owing to the fact that the bromate is reduced by nascent hydrogen, even in alkaline solution, and that with the bromide, it is not possible to entirely avoid the formation of hypobromite.

Solutions of potassium fluoride, when electrolysed under various

conditions, yield no evidence of the formation of any oxygen compound of fluorine; ozone is, however, always formed in considerable quantity.

T. E.

Influence of Time on the Process occurring at the Cathode in the Electrolysis of Solutions of Copper Sulphate. By CARL ULLMANN (*Zeit. Elektrochem.*, 1897, 3, 516—521).—The solutions were placed in a cylindrical cell the horizontal end faces of which consisted of copper plates which served as electrodes, a constant current was maintained, and the liquid disturbed as little as possible. When the current is allowed to pass through the cell, the E. M. F. remains fairly constant for a time, t , during which the copper is deposited in the compact form; the E. M. F. then rises suddenly and considerably, the deposit taking the form of a loose brown or black powder; and finally hydrogen gas is evolved, which disturbs the solution, causing the E. M. F. to diminish. The time, t , during which compact copper is deposited depends on the current density, D , and on the concentration of the solution, m , the relation $D\sqrt{t}/m = \text{constant}$, representing the author's experimental results with close approximation. Previous authors have found that for each concentration there is a limiting current density above which no coherent deposit can be obtained, but the author concludes that these observations are merely due to the fact that the time during which a coherent deposit is formed is too short to be observed. For example, Foerster and Seidel (*Abstr.*, 1897, ii, 243) found that in a 0.01 normal solution of copper sulphate a black deposit was obtained with 0.4 ampere per sq. dm., even though the solution was stirred; under these conditions, the author calculates that a coherent deposit would be obtained for 0.6 second in an undisturbed solution, so that, in order that the coherent deposit should be obtained permanently, the stirring should suffice to renew the layer of solution adjacent to the cathode at least once in 0.6 second.

T. E.

Electrolysis of Mixtures. By ANTON SCHRADER (*Zeit. Elektrochem.*, 1897, 3, 498—505).—The distribution of the current between two salts in a solution may, as Hittorf showed, be determined by means of migration experiments. Calling x the ratio in which the current is divided between the two salts, we have $x = Z_1 n_2 / Z_2 n_1$, where Z_1 and Z_2 are the increments in the concentrations of the anions at the anode (in equivalents) and n_1 and n_2 their migration constants. With potassium iodide and chloride, the ratio of the concentrations of iodine and chlorine at the anode is hardly changed by the electrolysis (a result already obtained by Hittorf), so that, since $n_1 = n_2$ in this case, the current is divided between the salts very nearly in the ratio of their concentrations.

In sufficiently dilute solutions the specific conductivity k is given by the equation $k = N_1 a_1 \lambda_1 + N_2 a_2 \lambda_2$, where N_1 and N_2 are the concentrations of the salts in gram equivalents per litre, a_1 and a_2 their dissociation coefficients in the mixture, and λ_1 and λ_2 their molecular conductivities at infinite dilution. Further, the current is divided between the salts in proportion to the number of ions and their mobilities, so that $x = N_1 a_1 \lambda_1 / N_2 a_2 \lambda_2$. By means of these two equations

and the values of α , it is therefore possible to calculate the dissociation coefficients of the salts in the mixture. Supposing the solutions to be made up by bringing together equal volumes of the solutions of the single salts, the dissociation after mixing is less than before. In the following table, the index 1 refers to potassium iodide.

N_1 .	N_2 .	N_1/N_2 .	α .	$10^8 k$.	After mixing.		Before mixing.	
					α_1 .	α_2 .	α_1 .	α_2 .
0·02595	0·02571	1·009	0·997	53·5	0·843	0·854	0·903	0·888
0·03442	0·04748	0·725	0·704	86·6	0·852	0·877	0·891	0·860
0·03074	0·06176	0·498	0·500	95·3	0·847	0·843	0·896	0·854
0·01992	0·03720	0·535	0·486	59·8	0·806	0·886	0·911	0·874

Mixtures of copper sulphate and sulphuric acid were examined in the same way; the following table contains the results obtained. The index 1 here refers to sulphuric acid.

N_1 .	N_2 .	α .	$10^8 k$.	After mixing.		Before mixing.	
				α_1 .	α_2 .	α_1 .	α_2 .
0·02753	0·06618	1·755	79·5	0·526	0·396	0·577	0·293
0·05297	0·12607	1·351	159	0·493	0·481	0·575	0·281
0·07217	0·07135	4·565	165·5	0·537	0·379	0·572	0·291
0·13753	0·24899	1·440	362	0·444	0·542	0·565	0·252
0·19605	0·34673	0·920	502	0·351	0·686	0·557	0·251
0·18043	0·14830	2·371	391	0·435	0·711	0·559	0·270

The interesting case of a mixture of acetic acid and silver acetate could not be examined, because the migration constant for acetic acid is not constant in solutions of a concentration with which it would be possible to work. The following values were obtained, v being the volume, in litres, in which a gram-molecule is dissolved, and n the migration constant for the anion.

v	1·267	1·357	1·703	2·077	2·789	3·988
n	0·362	0·307	0·241	0·212	0·182	0·169

The limiting value for infinite dilution should be 0·119.

From the values of α given above, it is possible to calculate the quantity of hydrogen which should separate at the cathode when a solution of sulphuric acid and copper sulphate is electrolysed; a part of this, however, is supposed to precipitate copper from the solution. The ratio, σ , between the latter part and the whole quantity which should separate out is a function of the current density. The author's results may be reproduced by an equation of the form $\sigma = A/(D + B)$, where A and B are constants and D is the current density. At a certain limiting current density, σ becomes equal to unity, and at lower current densities no hydrogen separates.

T. E.

The Electro-chemical Equivalent of Carbon. By ALFRED COEHN (*Zeit. Elektrochem.*, 1897, 3, 424—425).—When carbon is employed as the anode in the electrolysis of liquids which evolve oxygen, it is not only mechanically disintegrated but also chemically acted on, the nature of the latter action appearing to depend on the electrolyte employed. For example, a current of 0.12 ampère is passed through six cells furnished with anodes of pure carbon and cathodes of platinum, and containing sulphuric acid diluted with 1, 10, 20, 50, 100, and 500 volumes of water; after 10 hours, the most concentrated solution is colourless, the most dilute dark brown, and the others of intermediate shades of colour. At higher temperatures, there is less mechanical disintegration and the electrolyte is more strongly coloured than at lower temperatures. The mechanical disintegration is considerable at 100° in a solution containing equal volumes of water and concentrated sulphuric acid. A determination of the loss of weight of a carefully purified carbon anode under these circumstances gave the number 3.5 as the electrochemical equivalent of carbon, but some mechanical loss had occurred. A further series of determinations were made at the ordinary temperature with sulphuric acid diluted with from 10 to 500 times its volume of water, the particles of carbon lost mechanically being collected and their weight subtracted from the total loss of weight of the anodes. The electrochemical equivalent thus determined varied from 2.7 to 3.0. The number obtained is thus independent of the concentration or temperature of the acid, notwithstanding the apparent difference in the action. T. E.

Volatility of Fluorine Compounds. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, 16, 218—225).—The introduction of fluorine in the place of part of the hydrogen of a hydrocarbon appears to have but little influence on the boiling point of the compounds, this being raised, as a rule, some 5° by the substitution of 1 atom of fluorine for 1 of hydrogen. Benzene boils at 80°, phenylic fluoride at 84—85°; toluene boils at 111° and monofluorotoluene at 116°. If, however, fluorine is introduced into a molecule which already contains several halogen atoms, the boiling point is lowered, notwithstanding that the molecular weight is increased.

$\left\{ \begin{array}{l} \text{CHCl}_3 \\ \text{CFCl}_3 \end{array} \right.$	boils at	61°	$\left\{ \begin{array}{l} \text{CH}_2\text{Cl}_2 \\ \text{CHFCl}_2 \end{array} \right.$	boils at	41°
$\left\{ \begin{array}{l} \text{CH}_2\text{ClBr} \\ \text{CHFClBr} \end{array} \right.$	"	24°	$\left\{ \begin{array}{l} \text{CHCl}_2 \cdot \text{COCl} \\ \text{CFCl}_2 \cdot \text{COCl} \end{array} \right.$	"	14.5°
$\left\{ \begin{array}{l} \text{CHCl}_2 \cdot \text{COOH} \\ \text{CFCl}_2 \cdot \text{COOH} \end{array} \right.$	"	68°	$\left\{ \begin{array}{l} \text{CHCl}_2 \cdot \text{COOEt} \\ \text{CFCl}_2 \cdot \text{COOEt} \end{array} \right.$	"	107°
$\left\{ \begin{array}{l} \text{CHCl}_2 \cdot \text{CONH}_2 \\ \text{CFCl}_2 \cdot \text{CONH}_2 \end{array} \right.$	"	38°	"	"	75°
"	"	190°	"	"	157°
"	"	162.5°	"	"	130°
"	"	233°			
"	"	215°			

Also the substitution of fluorine for hydrogen in the aldehydic group $-\text{COH}$ causes a lowering of the boiling point.

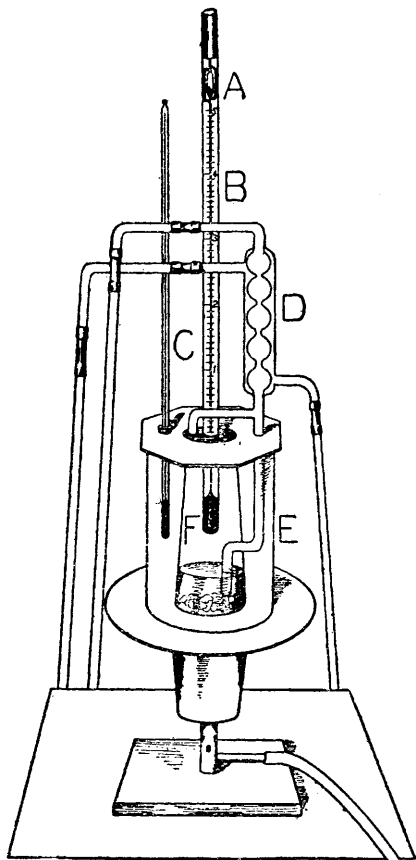
$\left\{ \begin{array}{l} \text{CH}_3 \cdot \text{COH} \\ \text{CH}_3 \cdot \text{COF} \end{array} \right.$	boils at	21°	$\left\{ \begin{array}{l} \text{C}_2\text{H}_5 \cdot \text{COH} \\ \text{C}_2\text{H}_5 \cdot \text{COF} \end{array} \right.$	boils at	49°
"	"	20.8°	"	"	44°
"	"		$\left\{ \begin{array}{l} \text{C}_5\text{H}_6 \cdot \text{COH} \\ \text{C}_5\text{H}_6 \cdot \text{COF} \end{array} \right.$	boils at	179°
"	"		"	"	154°

The author quotes numerous examples to show that the introduction of chlorine, in place of hydrogen, into compounds which already have several halogen atoms in the molecule, always increases the boiling point; a similar effect is also noticed when chlorine is substituted for the hydrogen of the aldehyde group.

J. J. S.

Modified Form of the Ebullioscope. By HARVEY W. WILEY (*J. Amer. Chem. Soc.*, 1896, 18, 1063—1067).—The flask F is closed by a rubber stopper carrying the large thermometer B and a tube leading to the condenser D. The vapours which are given off during ebullition are condensed in D and return to the flask through the tube, as indicated in the figure, entering the flask below the surface of the liquid therein. The flask is heated by a gas lamp and is placed on a circular disc of asbestos in such a way as to entirely cover the hole in the centre of the asbestos disc, which is a little smaller than the bottom of the flask. The whole apparatus is protected from external influences of temperature by the glass cylinder E, which rests on the asbestos disc below and is covered with a detachable, stiff rubber cloth disc above. The thermometer C indicates the temperature of the ambient air between F and E. The reading of the thermometer B should always be made at a given temperature of the ambient air, as indicated by C.

H. C.



New Method of Determining the Vapour Pressures of Solutions. By E. B. H. WADE (*Proc. Roy. Soc.*, 1897, 61, 285—287).—The apparatus employed in this research was, in conception, similar to that described by Sakurai (*Trans.*, 1892, 986), except that it was in duplicate, a divided steam supply passing through two U-tubes placed in parallel. The pressure on the contents of the two U-tubes, being the same, could be adjusted to any convenient value, and the method of thermometry being differential, the difference only of the boiling

points of pure water and of the solution in their respective U-tubes was recorded. The substances examined were the chlorides and bromides of potassium and sodium, and chlorides of lithium, calcium, and strontium. The results were compared with those calculated from the theory of Arrhenius; the discrepancy observed always exceeds the experimental error, except in the case of potassium chloride, and is particularly great in the case of calcium chloride.

H. C.

Vapour Pressure of a Substance compressed by a Gas that it Dissolves. By A. PONSOT (*Compt. rend.*, 1896, 123, 648—650).—From a mathematical consideration of the case of a solvent which is under the pressure of a gas that it dissolves, the author concludes that the gas or the dissolved substance in the liquid decreases the vapour pressure of the solvent, whilst, at the same time, the gas in the mixed vapour increases the vapour pressure of the solvent. The total effect is, therefore, that the vapour pressure increases if the gas is denser in the gaseous mixture than in the liquid mixture, and it decreases if the reverse is the case.

H. C.

Latent Heats of Vaporisation, and the Law of Van der Waals. By GEORGES DARZENS (*Compt. rend.*, 1897, 124, 610—612).—According to Van der Waals, $M\lambda/T_c = f(T/T_c)$, where M is the molecular weight, λ the latent heat of vaporisation at the absolute temperature T , T_c is the absolute critical temperature and f is a function which is the same for all substances. The author transforms this into $M\lambda/T = F(T/T_c)$, in which the first term is independent of the critical temperature, and then plots values of $M\lambda/T$ against those of T/T_c for different substances. All the curves $y = F(x)$ are of similar character; for low values of $x = T/T_c$ they are slightly concave towards the y axis, then at about $T/T_c = 0.750$ there is a point of inflexion, and the convex side is turned towards the y axis. No exact coincidence is obtained, the differences becoming more marked as the values of T/T_c decrease, and being probably partly due to errors in the determination of T_c , and to molecular association at low temperatures.

H. C.

Preliminary Experiments in the Determination of Vapour Density at Extremely High Temperatures. By VICTOR MEYER and MAX VON RECKLINGHAUSEN (*Ber.*, 1897, 30, 1926—1935).—The authors describe in detail the observations they have made in attempting to prepare a form of apparatus suitable for the determination of vapour densities at temperatures above 2000°. The material which resists most successfully the influence of these elevated temperatures is a commercial magnesia prepared from a magnesite occurring at Veitsch in Steyermark; this crude magnesia, on analysis, gave

MgO.	CaO.	MnO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	SiO ₂ .
88.2	0.9	0.6	7.1	0.8	2.4

When this substance is powdered, and converted into a paste with a cold, saturated solution of magnesium chloride, it becomes quite hard at the ordinary temperature after an interval of 1—2 days, the same effect being produced by exposure to a temperature of 120—150° during 1 hour. The oxychloride formed is completely decomposed and all the chlorine eliminated in the subsequent ignition.

Directions are given in the paper for preparing suitable vessels

from this material, but unfortunately, although vapour density flasks capable of resisting temperatures far above the melting point of platinum were obtained, it was not found possible to render them absolutely impervious to gases, although small pieces were burnt absolutely gas-tight. It is, however, hoped that this end may shortly be attained.
M. O. F.

Velocity of Solidification. By JACOB FRIEDLÄNDER and GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1897, 24, 152—159).—Tammann has previously shown (Abstr., 1897, ii, 444) that the velocity of solidification increases with the overcooling until a constant value is reached. The cause of the initial increase is probably due to differences in the disposition of the crystals and imperfect purity of the liquid, so that at first, with slight overcooling, the crystals are purer than the mother liquor, but when the maximum value is reached, solidification causes no change in concentration. Experiments were made with benzophenone, azobenzene, hydrocinnamic acid, diphenylamine, salol, benzoic anhydride and guaiacol, and curves showing the dependence of velocity on overcooling are given. For salol, the velocity is very small at all degrees of overcooling, but for all the other compounds it rapidly increases, and reaches a final constant value which differs very greatly for the different compounds, varying as it does from 570 for azobenzene to 6 for guaiacol.
L. M. J.

Method Pursued in Accurate Cryoscopic Determinations. By FRANÇOIS M. RAOULT (*Compt. rend.*, 1897, 124, 851—854).—The author details the precautions which must be taken in carrying out accurate cryoscopic measurements (compare Abstr., 1896, ii, 11, 88, and 362). He claims to have attained to an accuracy of 0.0005° in this work.
H. C.

Elevation of the Freezing Point in Benzene Solutions. By RÓZSA MIHÁLY (*Zeit. physikal. Chem.*, 1897, 24, 13—17).—When water is added to a solution of ethylic alcohol in benzene, the freezing point is raised, the elevation continuing until the water added reaches a very high percentage. Experiments were made with a solution containing originally about 23 per cent. of alcohol, with freezing point 1.74° , which leads to the value 4.83 for the association factor of the alcohol. A curve gives the effect produced on the freezing point by adding water, and exhibits a sharp bend at the point corresponding with $3C_2H_5 \cdot OH, H_2O$, but owing to the high association factor of the alcohol, the formation of this compound should not cause an elevation of the freezing point. Calculations of the freezing point on the assumption that the compound $9C_2H_5 \cdot OH, 3H_2O$ is formed are, however, found to agree satisfactorily with the observed numbers. Similar effects are obtained on adding water to solutions of phenol and acetic acid in benzene.
L. M. J.

Surface Tension of Water and of Dilute Aqueous Solutions. By N. ERNEST DORSEY (*Chem. News*, 1897, 76, 22).—The author has applied the method of ripples; these being produced by a fork, at a frequency of 62.87 double vibrations per second, on the water or solutions in a porcelain tray $1 \times 12 \times 14$ inches; the wave-length was

measured with a telescope, and the waves observed by Foucault's method. The water was distilled from chromic acid and alkaline permanganate, and the solutions varied in concentration from 0.05 normal to normal. The value found for water is $T = 75.98$ dynes per c.c. at 0° , and the values for dilute aqueous solution are linear functions of the concentration, and may be written $T_s = T_w + kC$, where T_s = surface tension of the solution, T_w surface tension of the water at the same temperature, k a constant, and C the concentration in gram-molecules per litre. The author's values for k are as follows: NaCl, 1.53; KCl, 2.23; $\frac{1}{2}\text{Na}_2\text{CO}_3$, 2.00; $\frac{1}{2}\text{K}_2\text{CO}_3$, 1.77; ZnSO_4 , 1.86. D. A. L.

Absorption of Nitrous Oxide in Aqueous Solutions of various Dissociated Compounds. By WALTHER ROTH (*Zeit. physikal. Chem.*, 1897, 24, 114—151).—From Gordon's experiments (Abstr., 1896, ii, 154) on the solubility of nitrous oxide in various solutions, an empirical equation was obtained for the lowering of the absorption coefficient, namely, $\alpha - \alpha_1/M^{\frac{1}{3}} = (\text{constant})$, where M is the number of gram-molecules of dissolved substance in unit volume of solution, that is, the lowering of the absorption coefficient is proportional to the number of salt molecules per square centimetre. As this law was not deduced theoretically, the author examined the conditions of equilibrium in the system and infers that the molecular concentration of the gas must be the same in pure water as in dilute solutions of a salt or indifferent compound, the assumptions involved being that there is no chemical action and that the molecular weight of the gas remains unaltered. In order to test the validity of this deduction, the author determined the absorption coefficient of nitrous oxide in pure water and in solutions of carbamide, glycerol, oxalic acid, phosphoric acid, and sodium chloride at various concentrations and at numerous temperatures varying from 4° to 25° . From the experimental results, an expression for the absorption coefficient of the form $\alpha - bt - ct^2$ is calculated and the values subsequently employed are derived from this expression. These and the density of the solutions give the ratio c/c_1 of the molecular concentrations of the gas in water and the solution. For carbamide, this ratio is equal to unity, the difference being irregular and only reaching 1 per cent., so that the law is valid. For glycerol, however, the ratio increases with the concentration and varies with the temperature, but as the cryoscopic behaviour of glycerol is also abnormal, the author considers it probable that, in more dilute solutions, the law would be obeyed. For oxalic acid solutions up to 3.7 per cent., the law is also valid, but for phosphoric acid and sodium chloride, it certainly does not hold good, even when the solutions are extremely dilute. The expression $\alpha - \alpha_1/M^{\frac{1}{3}}$ in these cases gives a constant, but with the glycerol solutions greater constancy is obtained for the expression $\alpha - \alpha_1/M$. L. M. J.

(NOTE.)—It may be noticed that the decrease of the absorption coefficient of the nitrous oxide is not in accord with Winkler's generalisation (Abstr., 1892, 556). L. M. J.

Decomposition of Salts by Water. By JOSEPH GUINCHANT (*Bull. Soc. Chim.*, 1896, [iii], 15, 555—560).—Salts of a strong acid and a weak base are decomposed by water, a basic salt being precipi-

tated, and the solution containing free acid and a residual salt, which may be either the normal or the basic salt. In the case of mercuric sulphate, if a complete decomposition of the normal salt into free acid and basic sulphate occurred under the influence of water, dissolution of the basic sulphate in dilute sulphuric acid, in which it might be expected to dissolve unchanged, would cause a depression of the freezing point of the acid solution. If the normal salt is only partially decomposed by water, and unchanged normal salt remains in the solution, dissolution of the basic sulphate in dilute sulphuric acid, with a portion of which it would combine, would raise the freezing point of the acid. The one effect actually produced is the one last mentioned, and as, moreover, the cryoscopic behaviour of the normal sulphate in dilute sulphuric acid is in keeping with the view that the mercuric sulphate dissolves unchanged, it appears that the decomposition of this salt by water is only a partial one.

H. C.

Dissociation in Solutions. By WALTER S. HENDRIXSON (*Zeit. anorg. Chem.*, 1896, 13, 73—80).—The distribution of a solid between two non-miscible solvents was studied, in the case of benzoic acid, with mixtures of water and benzene, and of water and chloroform, and in the case of salicylic acid with the same solvents. The author, applying Nernst's law (Abstr., 1891, 1148), obtains the dissociation coefficient of the double molecules into simple molecules in benzene and chloroform, from which the heat of dissociation of the double molecules can be calculated. Although the results are only approximate, it appears that the heat of dissociation is in both cases fairly large.

H. C.

Velocity of Oxidation of Gases by Liquids. By VICTOR MEYER and ERNST SAAM (*Ber.*, 1897, 30, 1935—1940).—The authors show that the absorption of hydrogen, carbonic oxide, and methane by solutions of potassium permanganate proceeds with uniform speed. The hydrocarbon is oxidised much less rapidly than hydrogen, and the speed of absorption diminishes in ascending the homologous series, propane and isobutane scarcely undergoing perceptible oxidation when agitated with a 5 per cent. solution of potassium permanganate during an hour.

Experiments were also performed with silver nitrate and silver oxide, but the results obtained with hydrogen exhibited less uniformity than in the case of potassium permanganate.

M. O. F.

Chemical Equilibrium between Ethylic Alcohol and Sulphuric Acid. By ARTHUR ZAITSCHEK (*Zeit. physikal. Chem.*, 1897, 24, 1—12).—By the mutual action of sulphuric acid and ethylic alcohol, or of the equivalent quantities of water and ethylic hydrogen sulphate, the same final state is reached, the action being reversible. The author has investigated, in solutions of various dilutions, the equilibrium constant for the bimolecular reaction $C_2H_5 \cdot OH + H_2SO_4 \rightleftharpoons C_2H_5 \cdot HSO_4 + H_2O$. The results do not give a constant value for k if the sulphuric acid be calculated as H_2SO_4 , but satisfactory constancy is obtained if it be calculated for H_2SO_6 , so that the author considers the sulphuric acid in aqueous solution to be present as the ortho-acid,

and no evidence is obtained of the existence of any higher hydrates. This apparently leads to the equation $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_5\cdot\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\cdot\text{HSO}_4 + 3\text{H}_2\text{O}$, that is, the decomposition of the sulphate is quadrimolecular, but the author considers the reaction to be really bimolecular, the sulphuric acid produced immediately forming the ortho-acid. In the presence of excess of acid, the mass law apparently does not hold, owing to the too rapid increase of velocity of the sulphate formation. No evidence of the formation of hydrates of either ethylic alcohol or of ethylic hydrogen sulphate was obtained. L. M. J.

Velocity of formation of Azo-dyes. II. By HEINRICH GOLDSCHMIDT and FRITZ BUSS (*Ber.*, 1897, 30, 2075—2093).—The equation given in the former paper (compare Goldschmidt and Merz, *Abstr.*, 1897, i, 278) represents the velocity of reaction between equivalent quantities of dimethylaniline hydrochloride and diazobenzenesulphonic acid in the presence of excess of hydrochloric acid; it also applies to diethylaniline, but in this case the velocity is somewhat smaller. By using salts of other acids, such, for instance, as trichloroacetic acid, the value of the constant becomes larger, although the dissociation constant of the acid is smaller. By the use of a weaker acid, such as acetic, chloroacetic, or dichloroacetic acid, a further complication arises, since the dissociation does not remain constant, but varies owing to the hydrolysis of the salt by the excess of acid present; in order to avoid this, a large excess of the weaker acid is necessary, but since the excess of acid has an influence on the velocity of reaction, the constants derived from the equations are not the true constants of velocity; in the case of strong acids, the product must be multiplied by the hydrolytic constant of the acid, and with weaker acids it must be multiplied by the hydrolytic constant and divided by the affinity constant. In this way, then, the affinity constants of the acids can also be determined, and the authors' figures in this respect correspond closely with those given by Ostwald. J. F. T.

An Improved Pyknometer. By EDWARD R. SQUIBB (*J. Amer. Chem. Soc.*, 1897, 19, 111—112).—The author has devised a specific gravity bottle which may be used at any temperature between 0° and 25°. The construction is that of the ordinary specific gravity bottle, but the stopper consists of a graduated stem with a safety reservoir at the top, the stem being ground into the bottle. The reservoir is closed by a stopper. L. DE K.

Inorganic Chemistry.

Critical Constants of Hydrogen Chloride, Phosphide, and Sulphide. By ANATOLE LEDUC and P. SACERDOTE (*Compt. rend.*, 1897, 125, 397—398).—The trihydrogen phosphide was prepared from a solution of cuprosodiphosphonium chloride, the hydrogen sulphide by

the action of hydrochloric acid on antimony sulphide. The following results were obtained :

	Critical temperature.	Critical pressure.
Hydrogen chloride	52°	83 atmos.
Hydrogen phosphide	52.8	64 „
Hydrogen sulphide	100	90 „

The results agree somewhat closely with those obtained by Dewar in the case of the chloride and sulphide, and also agree fairly well, so far as temperature is concerned, with the results of Vincent and Chappuis for the chloride, and of Olzewski for the sulphide, although there are considerable differences in the pressures. C. H. B

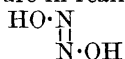
Hypiodous Acid and Hypiodites. By ROBERT L. TAYLOR (*Chem. News*, 1897, 76, 17—20, 27—29).—Schönbein found that ammonia decolorised an aqueous solution of iodine, yielding a liquid that bleached indigo and gave a blue colour with starch; the author confirms this statement and shows that similar solutions may be produced with potash, soda, lime-water, and barium hydroxide. The bleaching strength of such solutions, ascertained by titration with standard indigo-carmin, corresponds with the amount of iodine present, which amounts to about 1 per 5000; stronger solutions may, however, be prepared by using some precipitated iodine with the iodine water. These solutions decompose in a few hours at ordinary temperatures, and in a few minutes when boiled, with the production of the iodide and iodate. Acids decompose them with the liberation first of hydriodic and hypiodous or iodic acids, which at once react so that free iodine and water are obtained. With silver nitrate, the solutions yield a dark buff precipitate of the hypiodite mixed with hydroxide and iodide; with a cobalt solution, a black precipitate on standing; with a manganous salt, a dark brown precipitate immediately; with lead salts, a precipitate containing brown lead peroxide, and with hydrogen peroxide, an immediate and copious evolution of oxygen. The author has also obtained such solutions by Lunge and Schoch's method of triturating iodine, lime, and water together, and attributes their failure to delay in testing these solutions or to their having been heated. Moreover, solutions obtained by shaking mercuric oxide with iodine water are observed to have a feeble bleaching action, and on the addition of a drop of alkali, immediately become as active as the hypiodite solutions just referred to, which they then resemble in all other respects. These solutions of free hypiodous acid can be also made stronger if iodine is suspended in the iodine water; they can also be obtained by shaking iodine water with silver salts; in the latter case, however, they are very unstable, whilst when made by the use of mercuric oxide they are more stable than the hypiodite solutions. The free acid decomposes into hydriodic and iodic acids, which react and yield free iodine and water; it does not turn starch blue until after exposure to the air, but with silver nitrate it gives a precipitate consisting of the iodide, and iodate after boiling.

D. A. L.

Formation of Active Oxygen. By W. P. JORISSEN (*Ber.*, 1897, 30, 1951—1953. Compare Engler and Wild, *Abstr.*, 1897, ii, 402).—The author considers that the mechanism of oxidation by oxygen gas, in which a quantity of active oxygen equal to that concerned in the primary oxidation is produced, is not necessarily the same in all cases. The primary formation of a peroxide frequently affords the most simple explanation; whilst, on the other hand, cases may arise accompanied by electrical phenomena or by anomalies in the velocity of change which are best explained by van't Hoff's assumption of the dissociation of the oxygen molecule into oppositely charged ions (compare Jorissen *Abstr.*, 1897, ii, 253 and 487). T. E.

Reduction of Concentrated Sulphuric Acid by Copper. By CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1896, 18, 942—947. Compare *Abstr.*, 1896, ii, 474).—The author has repeated some of his former experiments, and now states that concentrated sulphuric acid (1.84) is reduced by copper when air is absent and at temperatures far below 86°, in fact, at ordinary atmospheric temperatures, with the formation of copper sulphate, cuprous sulphide, and sulphurous anhydride. The author also adheres to his previous statement that copper reduces concentrated sulphuric acid at 0° (compare Andrews, *Abstr.*, 1897, ii, 22). J. J. S.

Conversion of Nitrosohydroxylamines into Hyponitrous Acid. By ARTHUR R. HANTZSCH (*Ber.*, 1897, 30, 2356—2358).—Hyponitrous acid is formed by the direct action of nitrous acid on hydroxylamine in solution in methylic alcohol. It is also produced when dimethylnitrosohydroxycarbamide, $\text{NMe}_2 \cdot \text{CO} \cdot \text{N}(\text{OH}) \cdot \text{NO}$, which may also be regarded as isonitraminecarbamide, $\text{NMe}_2 \cdot \text{CO} \cdot \text{N}_2\text{O}_2\text{H}$, is treated with alkalis at 0°. From this it would appear probable that nitrosohydroxylamine and hyponitrous acid are tautomeric. The parallel formation of nitramide, $\text{N}_2\text{O}_2\text{H}_2$, from potassium nitrocarbamate, $\text{KO} \cdot \text{CO} \cdot \text{N}_2\text{O}_2\text{K}$, points to the probability that nitramide and hyponitrous acid are in reality stereoisomeric diazohydrates,



A. H.

Action of Arsenious Acid on Metallic Oxides, Oxychlorides, and Amidochlorides. By C. REICHARD (*Ber.*, 1897, 30, 1913—1916. Compare *Abstr.*, 1894, ii, 350).—The author has studied the behaviour of the oxides of copper, mercury, silver, nickel, cobalt, tin, chromium, manganese, and bismuth, copper oxychlorides, and the mercury ammoniochlorides towards solutions of arsenious oxide in water, soda, and ammonia. The observations, mainly qualitative, are embodied in a lengthy table, which does not admit of compression. M. O. F.

Characteristics of Flames. By NICOLAE TECLU (*J. pr. Chem.*, 1897, 56, 178—180).—Hirn (*Ann. chim. phys.*, 30, 319) has stated his inability to demonstrate optically the presence of particles of carbon in an ordinary gas flame, and concluded that at a high temperature these particles are transparent.

The author finds that when the shadows of a yellow and blue gas flame, a candle flame, and the flame from a petroleum lamp are thrown on to a screen and photographed, no difference is noticed in the case of the two gas flames, but a slight darkening in the shadow of the candle flame is observed, and a very marked one in the case of the petroleum flame.

The difficulty in obtaining the shadow of the particles in an ordinary luminous gas flame is due to their exceeding fineness. If, however, twelve fish-tail burners are placed one behind the other and lit up by an electric lamp, the darkening in their shadow is very pronounced. This cannot be caused by gases or vapours, because a layer of gas of the same thickness as the twelve fish-tail burner flame gave no shadow at all.

A. W. C.

NOTE BY EDITOR.—Soret (*Phil. Mag.*, 1875, p. 50), and Burch (*Abstr.*, 1885, 466) have incontestably proved that the flame of a candle contains solid particles.

Preparation and Properties of Potassium Percarbonate. By ARTHUR VON HANSEN (*Zeit. Elektrochem.*, 1897, 3, 445—448. See Constam and von Hansen, *Abstr.*, 1897, ii, 550).—The influence of small variations of temperature on the yield of potassium percarbonate is not very marked, if the specific gravity of the solution of potassium carbonate surrounding the anode is not allowed to fall below 1.52. Under these circumstances, the temperature may rise as high as 0° without sensibly affecting the yield. If the concentration falls, however, even a little below saturation, the yield of solid percarbonate suffers considerably, owing to the great solubility of the salt in more dilute solutions of potassium carbonate. High current density at the anode is also essential; with 0.5 to 2 ampères per sq. dcm., the product contains from 25 to 55 per cent. of percarbonate, whilst with 30 to 60 ampères per sq. dcm. it contained 85 to 95 per cent. The best results are therefore obtained by allowing a saturated solution of potassium carbonate to flow slowly into the anode compartment of the electrolytic cell at the bottom; the solution which has already undergone electrolysis, and in which the solid percarbonate remains suspended, floats on this and is slowly expelled from the cell, carrying with it the percarbonate; this is collected and dried on a porous plate in a current of dry air, which is finally warmed to about 40°. The yield of 87 to 93 per cent. salt is from 2.2 to 2.4 grams per ampère hour.

The salt is more stable than was at first supposed. When dry, it is only slowly decomposed at 100°, a temperature of 200° to 300° being required for its rapid decomposition. An aqueous solution decomposes slowly at the ordinary temperature, but rapidly at 45°. Completely dry potassium percarbonate may be preserved without undergoing appreciable change, but when moist it suffers somewhat rapid decomposition. It is very little soluble in alcohol, but extremely soluble in water, from which it cannot be recrystallised. It may, however, be purified by digestion at -5° to -10° with a concentrated solution of caustic potash; this dissolves the bicarbonate, and the remaining solid, after filtration and washing with alcohol, contains 95 to 99 per cent. of potassium percarbonate.

T. E.

Influence exercised by Ferric Oxide on the Formation of Sodium Sulphate from Sulphurous Anhydride, Air, and Sodium Chloride. By JEAN KRUTWIG (*Rec. Trav. Chim.*, 1897, 16, 173—180).—Iron pyrites was finely divided and thoroughly dried, and then mixed with finely divided common salt which had previously been heated to redness. The mixture, placed in a porcelain boat and introduced into a combustion tube, was heated in a Glaser furnace, while dried air was passed slowly through the tube; the air was then made to traverse tubes filled with glass wool, and finally through a tube containing a solution of potassium iodide. The first experiments were made with a mixture of pyrites and sodium chloride only; in later experiments, ferric oxide was introduced. The conclusions arrived at are: (1) ferric oxide acts as an oxygen carrier; (2) the conversion of sodium chloride into sodium sulphate depends on the amount of ferric oxide present; (3) the temperature at which the operation is carried on has a great influence on the results. J. J. S.

Silver Alloys. By GILBERT J. FOWLER and PHILIP J. HARTOG (*J. Soc. Chem. Ind.*, 1895, 14, 243—245).—The authors have attempted to prepare silver alloys which, whilst possessing the whiteness of silver, should not be liable to tarnish. The following alloys were obtained by fusing their constituents and then quickly cooling. Silver-zinc alloys:—1—Silver 95, zinc 5 per cent.; 2—silver 93, zinc 7 per cent.; 3—silver 90 and zinc 10 per cent. Silver-nickel alloys:—1—Silver 95 and nickel 4 per cent.; 2—silver 90 and nickel 10 per cent. Silver-nickel-zinc alloy:—silver 90, nickel 5, and zinc 5 per cent. Silver-copper-zinc alloys:—1—Silver 75, copper 15, and zinc 10 per cent.; 2—silver 67·87, copper 5·17, and zinc 27·47 per cent. Silver-aluminium alloy:—Silver 90 and aluminium 10 per cent. Silver-tin alloy:—Silver 95 and tin 5 per cent. All these alloys tarnished readily, but it was found that the stain was more easily removed by rubbing with a chamois leather than in the case of pure silver.

The authors also tried to obtain suitable alloys by electrolytic deposition from solutions containing silver and zinc; silver, zinc, and copper; or silver and aluminium, but the results were not satisfactory. (Compare S. P. Thompson, *Proc. Roy. Soc.*, 1887, 42, 387, and C. Winkler, this Journal, 1872, 1134). J. J. S.

Solubility of Calcium Sulphite in Water and in Sugar Solutions. By JULIUS WEISBERG (*Bull. Soc. Chim.*, 1896, [iii], 15, 1247—1250).—The calcium sulphite used was prepared by the action of sulphurous anhydride on milk of lime, and throughout the experiments care was taken to avoid contact with air as far as possible.

At 18°, a litre of water dissolves 0·043 gram of calcium sulphite only; a litre of a 10 per cent. sugar solution dissolves 0·0825 gram, and a litre of a 30 per cent. sugar solution dissolves practically the same amount. The sulphite in solution oxidises rapidly, especially if the solutions are heated. C. H. B.

Stability of Phosphorescent Strontium Sulphide. By JOSÉ R. MOURELO (*Compt. rend.*, 1897, 125, 462—464).—The various forms of phosphorescent strontium sulphide, when exposed to sunlight in presence of air, give off some hydrogen sulphide, and are more or less completely

oxidised. The least stable variety is that prepared by the action of hydrogen sulphide on the carbonate, and the most stable is that prepared by the author's modification of Verneuil's method (Abstr., 1897, ii, 450—469); the latter, in fact, changes very slowly. Impurities, more especially alkali compounds, increase the stability in all cases, most probably because they cause incipient fusion, and the sulphide thus becomes covered with a kind of protective glaze. In all cases, the rate of oxidation is more rapid if the sulphide is powdered, but the phosphorescence is not affected by the oxidation, except in so far as the sulphide is converted into non-phosphorescent compounds.

C. H. B.

Compounds of Metallic Hydroxides with Iodine. By THEODORE RETTIE (*J. Amer. Chem. Soc.*, 1897, 19, 333—339).—If a solution of a magnesium salt is mixed with a supersaturated solution of iodine in aqueous potash, or if it is first mixed with a solution of iodine in potassium iodide, and then with a small quantity of aqueous potash, a dark, reddish-brown precipitate is formed containing magnesium hydroxide and iodine.

The author now states that this compound must be considered rather as a mixture, since the ratio between the iodine and magnesium varies from 2.1 to 6.3. On substituting zinc acetate for a magnesium salt, an iodised zinc hydroxide is obtained in which the ratio between iodine and zinc is fairly constant, varying from 2.4 to 2.9. Cadmium nitrate also gives a fairly stable precipitate. The iodine is, however, only in a weak state of combination, and is gradually removed by washing or drying. (Compare Walker and Kay, Abstr., 1897, ii, 261.)

L. DE K.

New Mode of Combination between Metals: Alloys of Cadmium with Silver and with Copper. By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1896, [iii], 15, 1241—1247).—When a bar of cadmium is placed in a neutral solution of silver sulphate, the quantity of cadmium sulphate that is formed is exactly equivalent to the silver precipitated, but the loss of weight of the bar is much greater than the weight of the cadmium dissolved. Further, if the precipitated silver is allowed to remain in contact with the cadmium, the loss of weight of the latter increases during a period of five months or more, and in one set of experiments the loss was more than six times as great as the calculated amount. There is no decomposition of the water, and no appreciable formation of cadmium oxide, provided that air is excluded. Cadmium sulphate solution has no action on cadmium. If freshly precipitated silver is brought in contact with cadmium in presence of cadmium sulphate solution, similar results are obtained, and this is true also when pure water is substituted for the solution of the salt. The cadmium removed from the mass of the metal seems to combine with the finely divided silver, forming an alloy, and since the action practically ceases when the alloy has a composition corresponding with the formula AgCd_3 , it would seem that this is the limiting compound. The important point is, that the formation of this alloy is subsequent to, and not simultaneous with, the precipitation of the silver. Silver

acetate behaves like the sulphate, but with silver nitrate, the precipitated silver adheres so firmly to the cadmium that investigation becomes almost impossible.

Copper sulphate, chloride, and acetate yield similar results, with the exception that the formation of the cadmium alloy is simultaneous with the precipitation of the copper.

The velocity of the reaction varies with the different salts, but precipitation is completed more quickly the more dilute the solution. No hydrogen is liberated. The ratio of the excess of cadmium removed to the calculated quantity is independent of the quantity of copper solution used, but varies with its concentration; it is greater the more dilute the solution. These facts may be due to the existence of several definite alloys of copper and cadmium, or to an influence of the concentration of the solution on the proportion of the copper that is converted into alloy; the latter seems more probable. Copper nitrate, like silver nitrate, does not lend itself to experiments of this kind.

Cadmium precipitates all the lead from dilute solutions of lead acetate, but there is no evidence of any formation of an alloy. With solutions of lead nitrate, or concentrated solutions of the acetate, the precipitated metal adheres strongly to the cadmium.

C. H. B.

Improvements in the Preparation of Metallic Alloys by Electrolysis. By JOHANN WALTER (*Zeit. Elektrochem.*, 1897, 3, 385—388).—In the electrolytic preparation of alloys, it is difficult to obtain them in a homogeneous condition. To overcome this difficulty, one of the metals may be employed as cathode in the molten condition, and during the electrolysis, it should be stirred continuously; the same result may be obtained by allowing it to flow through the electrolyte in a thin stream. Secondly, the one metal may be suspended in the bath from which the other is deposited on it, the temperature of the bath being regulated so that the alloy formed fuses and falls to the bottom, exposing a fresh surface. A third process consists in periodically adding small quantities of the more readily separable metal to the bath; the two metals are then deposited in thin, alternate layers. A number of possible modifications of each of these methods is mentioned, and as examples of their application, the following processes are described. An *alloy of sodium and lead* may be obtained by using lead as the cathode in a bath of fused sodium chloride. The molten lead is stirred by passing through it some indifferent gas such as nitrogen, or, better, some gas which combines with the chlorine evolved at the anode, for example, hydrogen, carbonic oxide, or methane. An *aluminium-tin alloy* can be prepared by allowing tin to flow over a channelled carbon cathode forming the bottom of a bath of fused aluminium sodium chloride.

Silicon bronze is obtained by the electrolysis of fused sodium silicate, the melting point of which is preferably depressed by admixture of other suitable salts, a suspended rod of copper being employed as the cathode. The sodium formed reduces the silicate to silicon, which alloys with the copper; this alloy then fuses and drops down, exposing a fresh surface of copper.

Aluminium bronze can be prepared by adding cryolite and copper oxide or chloride alternately to a bath consisting of a mixture of sodium and potassium chlorides in fusion. The anode is of carbon, and the cathode of carbon or copper.

Sodium amalgam is obtained by the electrolysis of a solution of caustic soda, the mercury which is employed as cathode being allowed to flow slowly over a series of open gutters arranged in a terrace. If acetone, for example, be added to the liquid in the cathode compartment, it is reduced by the sodium amalgam to propylic alcohol.

T. E.

Compounds of Thallium. By LOUIS M. DENNIS and MARTHA DOAN (*J. Amer. Chem. Soc.*, 1896, 18, 970—977).—*Thallous trinitride*, TiN_3 , is obtained when a concentrated solution of potassium diazoate, containing a small quantity of the free acid, is added to a solution of thallous sulphate. It crystallises in fine needles, is strongly doubly refractive, and, in an atmosphere of carbonic anhydride, melts at 334° ; it is readily soluble in boiling water. When reduced in a current of dry hydrogen, it yields about 30 per cent. of its nitrogen in the form of ammonia.

Thallous thallic trinitride, $\text{TiN}_3\cdot\text{TiN}_3$, is most conveniently obtained by dissolving thallic hydroxide in diazoic acid (1.6 per cent. solution), and allowing the solution to stand at 0° in an exhausted Hempel desiccator; it crystallises in yellow or brownish crystals, which are highly explosive. Hot water decomposes the compound, part of the thallium being precipitated as thallic hydroxide, whilst part remains in solution and may be precipitated as thallous iodide.

Thallous tellurate, Ti_2TeO_4 , is obtained as a white, flocculent precipitate, sparingly soluble in water, on adding a solution of pure telluric acid to a solution of thallous hydroxide.

Thallous platinocyanide, $\text{Ti}_2\text{Pt}(\text{CN})_4$ (compare Carstanjen, *J. pr. Chem.*, 1867, 102, 144), crystallises in nearly colourless plates which are strongly doubly refractive.

J. J. S.

NOTE.—It has long ago been shown that the salt described by Carstanjen was a double carbonate and platinocyanide of thallium, and that thallous platinocyanide, when pure, is perfectly colourless. (Friswell, this Journal, 1871, 461; Friswell and Greenaway, *ibid.*, 1877, ii, 251).

Decomposition of Mercuric Sulphate by Water: Law of Thermochemical Moduli. By JOSEPH GUINCHANT (*Bull. Soc. Chim.*, 1896, [iii], 15, 1185—1191).—Varet's conclusion that mercuric sulphate dissolved in dilute sulphuric acid exists in the solution in the form of a hydrogen sulphate strictly comparable with the alkali hydrogen sulphates (Abstr., 1896, ii, 648), is not only contrary to the results of Ditte, Cameron, Le Chatelier, and other observers, but is contrary to the known chemical properties of the mercuric salts. The author points out that Favre and Silbermann's laws of thermochemical moduli are only approximate, and are not trustworthy criteria when dealing with questions of equilibrium. Moreover, Berthelot has shown that the laws only hold good in the case of strong bases, and are not

applicable at all to mercuric salts. All attempts to isolate a mercuric hydrogen sulphate have failed, and the fact that, when strong sulphuric acid is added to a solution of mercuric sulphate in dilute sulphuric acid, normal mercuric sulphate is precipitated, seems to show clearly that no hydrogen sulphate exists in the solution. Varet's observation, that the heat of dissolution of the sulphate in sulphuric acid is independent of the relative proportions of acid and salt and of the concentration of the acid, is analogous to Berthelot's in the case of potassium chloride and hydrochloric acid. Further, the author's own cryoscopic observations indicate that no mercuric hydrogen sulphate is formed in the solutions.

C. H. B.

Action of Fused Sodium Hydroxide under Pressure on Wrought Iron and Cast Iron. By AUGUSTE SCHEURER-KESTNER (*Bull. Soc. Chim.*, 1896, [iii], 15, 1250—1252).—Under pressure, the action of fused sodium hydroxide on iron is distinctly greater than under ordinary conditions. Whether under atmospheric or higher pressure, the amount of corrosion increases with the temperature, and wrought iron is attacked much more readily than cast iron. These observations are of considerable practical importance now that fusions with sodium hydroxide under pressure have frequently to be carried out, and it was, in fact, a serious accident due to rapid corrosion of an iron tube that directed the author's attention to the question.

C. H. B.

Chromium Tetroxide, and Salts of Perchromic Acid. By O. FRITZ WIEDE (*Ber.*, 1897, 30, 2178—2189).—If the blue solution obtained by extracting an aqueous solution of chromic anhydride and hydrogen peroxide with ether is cautiously treated with aqueous ammonia, the colour gradually disappears, and if the solution has been kept sufficiently cool, the under aqueous layer will have acquired a deep brown colour, and will deposit a greenish-brown precipitate on standing. This dissolves in warm 10 per cent. ammonia solution, and, on cooling, separates in the form of pale brown needles of a composition corresponding with the formula $\text{CrO}_4 \cdot 3\text{NH}_3$. This compound dissolves in water, undergoing partial decomposition, explodes when heated, and evolves oxygen on treatment with strong acids. When treated with alkalis, or if the ethereal solution itself is treated with a concentrated solution of a fixed alkali instead of ammonia, chromates of the alkali metals alone are formed. Other salts of perchromic acid can be prepared by employing substituted ammonias in place of ammonia. Thus, if the ethereal solution is treated with pyridine, and the ether evaporated in a brisk current of air, blue scales are left, and if one of these be introduced into the ethereal solution after the addition of the pyridine, long, dark blue, glistening prisms gradually separate having a composition corresponding with the formula $\text{CrO}_5\text{H}_4\text{C}_5\text{NH}_5$. They are extremely unstable, exploding violently even at the temperature of a hot summer's day; when dry, however, they can be kept in the cold for weeks, but in the presence of moisture rapidly decompose. The salt is soluble in almost all the neutral organic solvents, and is only gradually acted on by potassium permanganate in acid solution.

On adding aniline to the ethereal solution of perchromic acid, and diluting with an equal volume of light petroleum, dark red crystals, $\text{CrO}_5\text{H}, \text{NH}_2\text{Ph}$, separate, resembling potassium permanganate in appearance; this is even more explosive than the pyridine compound.

J. F. T.

Parastannyl Chloride. By RODOLPHE C. ENGEL (*Compt. rend.*, 1897, 125, 464—466).—When a solution of metastannic chloride (compare Abstr., 1897, ii, 376) in dilute hydrochloric acid is heated at about 100° for some time, it rapidly acquires the property of giving a precipitate with dilute sulphuric acid which is characteristic of the β -stannic chloride of Berzelius. No compound of definite composition could be isolated from the solution, but the product approximated in composition somewhat closely to metastannic chloride.

When metastannic acid is boiled with water, it is converted into the compound $\text{Sn}_5\text{O}_{11}\text{H}_2 + 7\text{H}_2\text{O}$, and when this is dried in a vacuum it yields the hydrate $\text{Sn}_5\text{O}_{11}\text{H}_2 + 2\text{H}_2\text{O}$. Neither of these hydrates dissolves in hydrochloric acid, and therefore they differ from metastannic acid; they combine with it, however, and when the product has been dried on porcelain, it dissolves in water, and the opalescent solution gives a precipitate with sulphuric acid, but is very slowly precipitated by excess of hydrogen sulphide. The dried chloride, which has the composition $\text{Sn}_5\text{O}_9\text{Cl}_2 + 2\text{H}_2\text{O}$, is decomposed by excess of water, and the product, when dried, has the composition $\text{Sn}_5\text{O}_{11}\text{H}_2 + 2\text{H}_2\text{O}$, its potassium salt crystallises with $3\text{H}_2\text{O}$, and from it the corresponding chloride can be prepared by the action of hydrochloric acid.

The author distinguishes these compounds as parastannic compounds, and their relation to the metastannic compounds is shown in the following table.

	Dried in Air.	Dried at 100° .	Chloride.	Potassium Salt.
Metastannic ...	$\text{Sn}_5\text{O}_{11}\text{H}_2, 9\text{H}_2\text{O}$	$\text{Sn}_5\text{O}_{11}\text{H}_2, 4\text{H}_2\text{O}$	$\text{Sn}_5\text{O}_9\text{Cl}_2, 4\text{H}_2\text{O}$	$\text{Sn}_5\text{O}_{11}\text{K}_2, 4\text{H}_2\text{O}$
Parastannic ...	$\text{Sn}_5\text{O}_{11}\text{H}_2, 7\text{H}_2\text{O}$	$\text{Sn}_5\text{O}_{11}\text{H}_2, 2\text{H}_2\text{O}$	$\text{Sn}_5\text{O}_9\text{Cl}_2, 2\text{H}_2\text{O}$	$\text{Sn}_5\text{O}_{11}\text{K}_2, 3\text{H}_2\text{O}$

The contradictory statements of earlier investigators are probably attributable to the fact that they were dealing with mixtures of the different modifications of the stannic compounds.

C. H. B.

Mineralogical Chemistry.

Crystalline Form and Composition of Boulangerite. By S. A. HJALMAR SJÖGREN (*Geol. För. i Stockholm Förh.*, 1897, 19, 153—167). —Boulangerite has long been known at Sala in Sweden, but has not previously been analysed. It occurs as acicular and capillary crystals embedded in calcite. On dissolving the calcite, striated needles are isolated which are shown to be orthorhombic and to have parameters agreeing with those of diaphorite.

	a	:	b	:	c
Boulangerite, $5\text{PbS}, 2\text{Sb}_2\text{S}_3$	0.5527	:	1	:	0.7478
Diaphorite, $5(\text{Pb}, \text{Ag}_2)\text{S}, 2\text{Sb}_2\text{S}_3$	0.4919	:	1	:	0.7346

The analysis by R. Mauzelius agrees with the formula $5\text{PbS}, 2\text{Sb}_2\text{S}_3$, showing the mineral to be isomorphous with diaphorite.

Pb.	Ag.	Zn.	Sb.	S.	Insol. (silicate).	Total.	Sp. gr.
55.22	trace	0.06	25.54	18.91	0.23	99.96	6.185

The formula always accepted for boulangerite, namely $3\text{PbS}, \text{Sb}_2\text{S}_3$, was first given when the atomic weight of antimony was not exactly known. From a re-calculation of all the previous analyses, the iron, copper, &c. being taken as replacing lead, it is found that the majority agree with the formula $5\text{PbS}, 2\text{Sb}_2\text{S}_3$, whilst none agree exactly with $3\text{PbS}, \text{Sb}_2\text{S}_3$. The first of these formulæ has previously been given by Zepharovich (1867) and Eakins (1888) for sulphantimonites of lead from Przibram and Colorado respectively. From Frenzel's analyses (1870), embrithite and plumbostibiite are made a distinct species under the name embrithite, with the formula $10\text{PbS}, 3\text{Sb}_2\text{S}_3$.

L. J. S.

Vanadium in Rutile. By C. BERNHARD HASSELBERG (*Chem. News*, 1897, 76, 102—104, 112—113; from *Astrophysical Journ.*, 1897, 5, 194; 6, 22—26, and *Bihang Svenska. vetensk. Akad. Handl.*, 22, (1), No. 7).—For the purpose of mapping the lines in the arc-spectrum of titanium, rutile was the material at first employed, since this mineral is usually considered to contain, as a rule, only iron in addition to titanic acid. The lines of vanadium and chromium were, however, prominent in the spectra of several rutiles from various localities. Nordenskiöld has recently confirmed the presence of vanadium in Norwegian rutile by ordinary chemical analysis.

WILLIAM B. GILES (*Chem. News*, 1897, 76, 137) points out that Sainte-Claire Deville was the first to detect vanadium in rutile (*Compt. rend.*, 1859, 49, 210; *Ann. Chim. Phys.*, 1861, 61, 309; *Chem. News*, 1861, 2).

L. J. S.

Artificial Production of Laurionite and of Isomorphous Compounds. By AUGUST B. DE SCHULTEN (*Bull. Soc. fran. Min.*, 1897, 20, 186—191).—Laurionite, an orthorhombic oxychloride of lead, $\text{PbCl}\cdot\text{OH}$, found in the old lead slags of Laurion, Greece, may be prepared artificially as follows. To a boiling solution of 1000 grams of neutral lead acetate in 2.5 litres of water is added a hot solution of 50 grams of sodium chloride in 250 c.c. of water; the mixture is quickly filtered, and the filtrate heated on the water bath for 12 to 16 hours, when a deposit of well crystallised laurionite is formed. The crystals are slowly attacked by cold, but more quickly by hot, water. When heated at 100° , they are not affected, but at a low red heat they lose water and melt. The orthorhombic crystals are colourless and transparent with an adamantine lustre, the largest being 1—2 mm. in length and 0.1 mm. in thickness. The observed angles agree closely with those of the natural crystals. Similar crystals are also deposited from a cold solution of sodium chloride and lead acetate, the latter being in excess.

	$a : b : c$	Sp. gr.
$\text{PbCl}\cdot\text{OH}$	0.7366 : 1 : 0.8237	6.241
$\text{PbBr}\cdot\text{OH}$	0.7310 : 1 : 0.8043	6.721
$\text{PbI}\cdot\text{OH}$	0.7476 : 1 : 0.8081	6.827

The corresponding bromine and iodine compounds are obtained in yellow crystals by the same methods, using sodium bromide and potassium iodide instead of sodium chloride, and in the latter case in the presence of free acetic acid. Analyses of crystals of the three compounds agree closely with the formulæ.

L. J. S.

Artificial Phosgenite and Bromophosgenite. By AUGUST B. DE SCHULTEN (*Bull. Soc. fran. Min.*, 1897, 20, 191—193).—Friedel and Sarasin have prepared phosgenite by heating lead chloride and carbonate with water, in a sealed tube at 180°. The natural occurrence, however, suggests that the mineral has been formed at the ordinary temperature.

It may also be obtained at the ordinary temperature by passing a current of carbonic anhydride over an aqueous solution of lead chloride; the bright tetragonal crystals thus formed are about 0.16 mm. across, they have the composition $\text{PbCO}_3 \cdot \text{PbCl}_2$ and sp. gr. 6.134. Those formed on the surface of the liquid are pyramidal in habit, $x\{111\}$ predominating, whilst on those deposited at the bottom $c\{001\}$ predominates.

The corresponding bromine compound is obtained by passing carbonic anhydride over a solution of lead bromide; the colourless, transparent crystals have the same crystallographic and optical characters as the chlorocarbonate; sp. gr. 6.550. Attempts to prepare the corresponding iodine compound were not successful.

L. J. S.

Simultaneous Production of Laurionite, Phosgenite, and Cerussite. By AUGUST B. DE SCHULTEN (*Bull. Soc. fran. Min.*, 1897, 20, 194—195).—Laurionite, phosgenite, and cerussite occur in association at Laurion, Greece, having been formed by the action of sea water and air on the old lead slags. The three minerals may be artificially produced together by passing a slow current of carbonic anhydride over a solution of 20 grams of normal lead acetate and 2 grams of sodium chloride in a litre of water. Bright crystals of laurionite soon make their appearance on the sides of the flask and on the surface of the liquid; shortly afterwards crystals of phosgenite are also formed, and still later cerussite is produced, apparently at the expense of the laurionite. The small twinned crystals of cerussite show the forms $p\{111\}$ and $m\{110\}$, and are deposited on the phosgenite. Experiments made on artificial laurionite and phosgenite show that, in the presence of carbonic anhydride and water, laurionite is transformed into phosgenite, which in turn is itself transformed into cerussite.

L. J. S.

Crystallised Cadmium Carbonate and Artificial Dialogite [Rhodochrosite]. By AUGUST B. DE SCHULTEN (*Bull. Soc. fran. Min.*, 1897, 20, 195—198).—Rhombohedra of cadmium carbonate have been prepared by Bourgeois (1887), but attempts to obtain it by Senarmont's method have resulted in the formation of cadmium oxychloride. The method now used consists in adding excess of ammonium carbonate to a solution of cadmium chloride, and then just enough ammonia to dissolve the precipitate of cadmium carbonate; on heating this solution on the water bath, bright crystals of the

composition CdCO_3 are deposited as the ammonia is driven off. The transparent crystals, 0.1—0.2 mm. across, are simple rhombohedra with the angle $\alpha' = 74^\circ$ about; sp. gr. 4.960.

Manganese carbonate has been obtained in the form of a crystalline powder by Senarmont, and the method described above yields it as rhombohedra, but it is liable to oxidation; another method is to boil a solution of precipitated manganese carbonate in water saturated with carbonic anhydride. The bright crystals, which have the composition MnCO_3 , are simple rhombohedra 0.03 mm. across; $\alpha' = 73^\circ 25'$; sp. gr. 3.65. On heating these crystals of cadmium carbonate and manganese carbonate, they are converted into black oxide without change of external form. L. J. S.

Ferric Sulphate in Mine Waters, and its Action on Metals. By L. J. W. JONES (*Proc. Colorado Sci. Soc.*, 1897 [read June 5], 9 pp.).—Water from the Stanley mine, at Idaho Springs, Colorado, contains in parts per thousand.

SiO ₂ .	NaCl.	Na ₂ SO ₄ .	K ₂ SO ₄ .	Al ₂ (SO ₄) ₃ .	ZnSO ₄ .	
0.0438000	0.0134500	0.3117200	0.1554800	0.0197870	0.1224400	
MnSO ₄ .	MgSO ₄ .	CaSO ₄ .	Fe ₂ (SO ₄) ₃ .	FeSO ₄ .	CuSO ₄ .	Total.
0.4271400	0.4674600	0.6362900	0.6033600	0.0093370	0.1918010	3.0020650

The water deposits a muddy brown sediment, which is shown by the following analysis, made on material dried at 100° , to be a hydrated basic ferric sulphate.

Fe_2O_3	Al_2O_3	SiO_2	SO_3	H_2O	Total.
53.57	2.87	10.85	11.46	21.14	99.89.

The water has a strongly acid reaction, but contains no free acid; it very quickly corrodes the pumping apparatus, especially iron and copper, but bronze more slowly. Experiments showed that several metals are acted on by ferric sulphate solution. L. J. S.

Pyrophyllite from Colombia. By AUGUSTIN A. DAMOUR (*Bull. Soc. fran. Min.*, 1897, 20, 183—185).—The emeralds of Muso, near Bogota, occur in a crystalline limestone, accompanied by a black, carbonaceous shale, and in association with parisite, pyrites, anthracite, and pyrophyllite. The anthracite has sp. gr. 1.64. The pyrophyllite occurs in greenish-white, flattened nodules with a fibrous structure. Analysis agrees approximately with the usual formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$.

SiO_2	Al_2O_3	Fe_2O_3	CaO, MgO	H_2O and volatile matter.	Total.
63.56	29.16	1.68	traces	6.36	100.76

L. J. S.

Stolzite and Raspite from Broken Hill. By CARL HLAUATSCH (*Ann. k.k. naturh. Hofmuseums Wien*, 1897, 12, 33—41; and *Zeits. Kryst. Min.*, 1897, 29, 130—139).—Transparent, light yellow, red, and brownish crystals of stolzite occur on galena, limonite, and psilomelane at Broken Hill, New South Wales. Five types of tabular and pyramidal crystals are described, and several new forms noted;

$a:c = 1:1.5606$; the tetragonal crystals show the usual parallel hemihedrism, and are not hemimorphic; they are uniaxial and negative; for sodium light $\omega = 2.2685$, $\epsilon = 2.182$. Analysis by F. P. Treadwell gave I.

	WO ₃ .	PbO.	MnO.	MgO.	Fe ₂ O ₃ + MnO.	Total.
I.	51.34	47.44	0.78	trace	—	99.56
II.	49.06	48.32	—	—	1.43	98.81

The new mineral raspite is found on some of the stolzite specimens as brownish or yellow monosymmetric crystals with a strong adamantine lustre. They are flattened parallel to $a(100)$, and elongated in the direction of the axis of symmetry; $a:b:c = 1.3493:1:1.1112$; $\beta = 72^\circ 19'$. There is a perfect cleavage parallel to $a(100)$, and the crystals are always twinned on this plane. The plane of the optic axes is $b(010)$; the index of refraction is very high, being about 2.6. Hardness, $2\frac{1}{2}$ —3. Analysis II, by Treadwell, gives the formula PbWO₄, showing the mineral to be dimorphous with stolzite; it may possibly be isomorphous with wolframite. L. J. S.

The Oscuro Mountain Meteorite. By RICHARD C. HILLS (*Proc. Colorado Sci. Soc.*, 1897 [read April 3], 4 pp.).—Three masses of this iron were found in December, 1895, close together on the Oscuro Mountains, Socorro Co., New Mexico, weighing respectively 1467, 1226, and 676 grams. There is no sign of weathering. Etching develops distinct Widmanstätten figures. Graphite and schreibersite are present, but no troilite was observed. Analysis gave

Fe.	Ni.	Co.	P.	C.	Total.
90.79	7.66	0.57	0.27	0.07	99.36

Other irons recently described from South Central New Mexico are the El Capitan (Abstr., 1896, ii, 193), and the Sacramento Mountains (Abstr., 1897, ii, 218). L. J. S.

Composition of the Louisville Mineral Water. By EDGAR H. S. BAILEY (*Kansas Univ. Quart.*, 1897, 6, A, 117—119).—Water issuing from limestone at Louisville, Pottawatomie Co., Kansas, has a temperature of 56° F.; at first it is quite clear, but soon becomes yellow and turbid. It has an astringent taste. Analysis gave, in 100,000 parts,

Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	SO ₃ .	Cl.	SiO ₂ and insol.	CO ₂ .
2.84	38.17	9.32	8.05	0.52	12.89	3.85	4.64	99.90

Also traces of nitric acid and organic matter. Several waters of Kansas have more magnesium than this, but as they also contain much sodium chloride, they are not palatable. The Saline river contains more mineral matter in solution than the water of this spring. L. J. S.

Physiological Chemistry.

Absorption of Oxygen by the Lungs. By JOHN S. HALDANE and J. LORRAIN SMITH (*J. Physiol.*, 1897, 22, 231—258).—The absorption of oxygen in the lungs cannot be explained by diffusion alone, as the normal oxygen tension in the blood is higher than in the alveolar air, and in some animals higher than in the atmosphere. Fall of body temperature caused a marked fall in this tension. Increase of oxygen in the alveolar air causes an almost proportional increase in the oxygen tension of the arterial blood. Diminution of the oxygen tension in the alveolar air causes a fall in that of the blood; but want of oxygen, whether produced by carbonic oxide poisoning, by diminution of atmospheric pressure, or of percentage of oxygen in the air, causes a marked increase in the *relative* excess of arterial over alveolar oxygen tension. Hence want of oxygen acts as a stimulus to absorption of oxygen. The symptoms caused by diminution of the oxygen tension of the air breathed are due to fall in the oxygen tension reached by the blood in the lungs, and not to diminution in the quantity of oxygen carried by the blood from the lungs.
W. D. H.

Metabolism during Inanition. By DAIBER (*Chem. Centr.*, 1896, ii, 1039, from *Schweiz. Woch. Pharm.*, 34, 395—399).—Observations made on Succi during a 20 days' fast showed that the body weight sank about 490 grams daily, the excretion of chlorides in the urine fell to 1 or 1.5 per cent. of the normal; chlorides were not found in the urine on the twentieth day. At the beginning of the fast, urobilin was abundant, indicating decomposition of the red blood corpuscles. The metabolism of proteid as indicated by the discharge of urea was very regular.
W. D. H.

Influence of the Thyroid Gland on Metabolism. By BERNHARD SCHÖNDORFF (*Pflüger's Archiv.*, 1897, 67, 395—442).—By feeding dogs on thyroid, they are reduced in weight; this is due to loss of fat, and the amount of oxygen used is increased. When the body fat has sunk to a certain point, the proteid of the body is attacked. When the animal resumes normal diet, metabolism falls, fat and proteid are put on, and the body weight rises; renewed administration of thyroid is then followed by no increase in the excretion of nitrogen.

During menstruation in women, and the corresponding period in dogs, the proteid metabolism sinks. During hunger, the rise of nitrogenous excretion which occurs late in the process is not always coincident with the greatest deficit in fat; the organs become richer in water.
W. D. H.

The Assimilation of Iron. By EMIL HÄUSERMANN (*Zeit. physiol. Chem.*, 1897, 23, 555—592).—Analyses of various foods are given, from which it appears that the seeds of cereals are even poorer in iron than milk. Rats, rabbits, and dogs were fed on food poor in iron, and others on the same, *plus* inorganic compounds of iron, and in one series (on rats) hæmoglobin was added instead; in the last, the hæmoglobin

of the blood rose considerably, although not so high as when a normal mixed diet was given. There was an increase of iron in the body, but no important increase in hæmoglobin in rats and rabbits after the administration of inorganic salts of iron; in dogs, as also in man, the hæmoglobin increases. This, however, as the author admits, hardly settles the question whether the hæmoglobin formed comes from the iron given.

W. D. H.

Analyses of Blood. By EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1897, 23, 521—531).—Two very complete analyses of the blood, one of the ox, the other of the horse, are given.

W. D. H.

Coagulating Action of Gelatin on the Blood. By A. DASTRE and N. FLORESCO (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 243—245).—If gelatin dissolved in solution of sodium chloride is injected into a vein of a dog, the gelatin is excreted in the urine, and the urine gelatinises on cooling. The blood, when withdrawn, coagulates with great rapidity. If, however, the blood is mixed with decalcifying agents such as potassium oxalate, it does not clot; but gelatin annuls the anti-coagulating power of proteoses (pro-peptone).

W. D. H.

Glucose in the Blood and Muscle after Intra-venous Injection of that Substance. By L. BUTTE (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 274—277).—After the intra-venous injection of large doses of glucose, it is excreted by the urine for about 36 hours; it is, however, not found for long in the blood, disappearing from it in about 50 minutes to 2 hours. In the muscles, also, it disappears as rapidly. It appears that of the sugar injected some is excreted, some is used immediately for purposes of combustion, and a third part probably undergoes "transformation" in certain organs.

W. D. H.

Origin of Fat in Animals. By MAURICE KAUFMANN (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 414—417).—All the proximate principles of food may serve for the formation of fat. In carnivora, it originates from the proteid and fat of the food; the fat, however, is principally indirectly concerned in fat-production by preserving from oxidation the fat already stored from proteid.

W. D. H.

Transformation of Fat into Glycogen. By SABRAZÈS (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 239—243).—A case of fibro-lipoma growing from the mucous membrane of the mouth is described; this showed the presence of glycogen in the ulcerated portions. The glycogen was especially abundant in the leucocytes; this is believed to be due to the intracellular digestion of the fat of the tumour.

W. D. H.

Breaking up of Fat in the Alimentary Canal. By VAUGHAN HARLEY (*Proc. Roy. Soc.*, 1897, 61, 249—265).—The absorption of milk-fat in normal dogs is compared with that in those from which the pancreas had been removed; the difference in the amount of fat left in different portions of the alimentary canal is not so great as would have been anticipated. Hydrolysis of fats into fatty acids and glycerol occurs in the stomach, as also does saponification; this is

greater in dogs without a pancreas, and is probably explained by the fact that, in these animals, the expulsion of fat into the intestine is delayed.

W. D. H.

Cholesterol in the Bile. By DOYON and E. DUFOURT (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 487—489).—Doubt exists as to whether cholesterol is formed by the liver cells or by the biliary passages. It has a double origin; fistula bile contains cholesterol, but in less quantity than bladder bile.

W. D. H.

Mechanism of Organic Oxidation. By J. E. ABELOUS and G. BIARNÈS (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 94—96).—Two experiments are described which show that at the same time that salicylaldehyde is oxidised into salicylic acid as the result of digestion with aqueous extracts of liver, oxygen is consumed and carbonic anhydride disengaged; the extract was rendered antiseptic by chloroform. The same result follows if a solution of the precipitate produced by the addition of alcohol to the liver-extract is used instead. The "oxidising" ferment thus adheres closely to the protoplasm of the liver cells.

W. D. H.

The Importance of Nucleo-proteids in the Oxidative Processes of Cells. By WILHELM SPITZER (*Pflüger's Archiv.*, 1897, 67, 615—656).—The various tissues and organs of the body have an oxidising energy which was principally investigated in the present research by the amount of oxygen formed from hydrogen peroxide. In some cases, other tests, such as the conversion of salicylaldehyde into salicylic acid, were used as well. In their order of activity, the tissues are thus arranged, blood, spleen, liver, pancreas, thymus, brain, muscle, ovary, oviduct, the most active being placed first; this list nearly coincides with those given by Abelous and Biarnès, and by Salkowski.

The action is destroyed by protoplasmic poisons, like potassium cyanide and hydroxylamine. It is not influenced by cold to any noteworthy extent, its optimum is at 30—50°, and it is completely destroyed by heating to 70°.

The substance on which this property depends is only partially extracted by water; to say that it is an enzyme is no explanation. A definite search was made as to whether or not it depends on nucleo-proteid, and the answer was in the affirmative. Nucleo-proteids were prepared from various organs and tissues by the methods given by different authors, and all were found to have the oxidising energy of the original tissue or organ; these compounds are affected by poisons and temperature like the original organs. Numerous analyses of various nucleo-proteids are given, and considerable importance in this connection is given to the constant presence of iron in them. The glycolytic power of the blood is attributed to the same substances.

W. D. H.

Cerebro-spinal Fluid. By E. NAWRATZKI (*Zeit. physiol. Chem.*, 1897, 23, 532—554).—Previous workers on cerebro-spinal fluid have all but unanimously stated that the reducing substance contained in it is not sugar. In the present case, large quantities of the fluid were

obtained from calves and horses, and also from men ; the author thus regards his work as being more trustworthy than that of others, who mostly worked with small quantities. Although he was not successful in separating the sugar in the crystalline form, he states that otherwise the reducing substance gives all the reactions characteristic of dextrose. He did not find catechol, as Halliburton did. In the fluids he examined, globulin was the only proteid present, proteoses and peptones being absent. The sugar in cerebro-spinal fluid disappears soon after death (glycolytic action).

W. D. H.

Behaviour of Compounds of Salicylic Acid in the Organism.

By STANISLAS BONDZŃYSKI (*Chem. Centr.*, 1896, ii, 1039—1040; from *Arch. exp. Path. Pharm.*, 38, 88—98).—After the use of sodium salicylate, 97·5 per cent. of it was found in the urine as salicyluric acid; after the use of ethylic salicylate, 91·3 per cent. was found in the urine. After ethylenic salicylate, 47·6 per cent. was found in the urine as salicyluric acid, and 19·5 per cent. in the fæces as salicylic acid. Of salicylglyceride, 86·7 per cent. passes unchanged through the alimentary canal, and 8·7 per cent. is excreted in the urine as salicyluric acid. Dichlorhydrin-salicylate appears chiefly in the urine (92·7 per cent.). After the use of salicyl compounds soluble in water, such as salicylamide, there was complete absorption, none being found in the fæces.

W. D. H.

Physiological Action of Nicouline. By ED. BOINET (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 403—406).—*Nicouline*, C_3H_4O , a colourless, inodorous substance crystallising in rhomboidal tablets, was extracted by Geoffroy from *Robinia Nicou Aublet*, a leguminous plant used by the natives of Guiana to stupefy and capture fish.

The action of nicouline is on the central nervous system, especially on the bulb ; after a phase of excitation, stupor sets in, the muscles are relaxed, sensation is in abeyance, and the temperature falls. It is rapidly eliminated. The fatal dose for mammals is 1 milligram per 10 grams of the body weight.

W. D. H.

Action of Scopoline and Scopolectines. By ARNOLD SCHILLER (*Chem. Centr.*, 1896, ii, 1039; from *Arch. exp. Path. Pharm.*, 38, 71—87).—Scopoline, on account of its insolubility, does not act on frogs, but the scopolectines (cinnamylscopoline, benzoylscopoline, acetylscopoline) produce narcosis, with a rise of reflex irritability. The cinnamyl compound is the most active, 0·01—0·02 gram producing a marked effect ; in rabbits and cats, however, 0·12 gram produces no corresponding results. In contradistinction to scopolamine, scopoline and the scopolectines produce no effect on the pupil, secretion of saliva, or vagus endings in the heart.

W. D. H.

Physiological Action of Copper. By ARNOLD KOLDEWEY (*Chem. Centr.*, 1896, ii, 1041; from *Dissert. Berlin*).—Although it is advisable to obviate admixture of copper with the food, no noteworthy evil results follow small doses of copper, or even large doses in people in good health, or in animals that vomit readily ; long continuance in the use of copper, however, produces slight degenerative changes in the liver and kidney, which can only be detected on microscopic examination. The

existence of chronic copper poisoning among workers in that metal is doubted, and illness, if it occurs, is probably to be attributed to arsenic, zinc, or lead mixed with the copper. W. D. H.

Composition of Normal Urine. By CHARLES PLATT (*J. Amer. Chem. Soc.*, 1897, 19, 382—384).—The amounts of the various constituents of the urine of men and women are arranged in a lengthy table. The numbers given are averages compiled from the observations of the author (number not stated) and those of forty-eight other investigators; they do not differ in any essential particular from those found in the text-books. W. D. H.

Excretion of Phosphorus during Feeding with Casein. By GOTTHELF MARCUSE (*Pflüger's Archiv.*, 1897, 67, 373—394).—The experiments were carried out in the usual manner of metabolism experiments; a dog was used, and the phosphorus in its food (casein and meat extract), and in its excrements, was estimated. In four experiments, the average of phosphorus absorbed from the food was 90 per cent. of that given; this is even better than when meat is given. The phosphorus thus follows the same course as was previously shown in the case of the nitrogen of casein, thus confirming the view, previously found expressed, of the high nutritive value of casein. W. D. H.

Nitrogenous Excretion in Phloridzin-diabetes. By CH. CONTE-JEAN (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 344—347).—In phloridzin-diabetes in animals, the excretion of nitrogen is not increased, as von Mering states, and proteid cannot therefore be regarded as the precursor of sugar. The opinion expressed is that the sugar is formed, partly, if not exclusively, from the fat of the organism. W. D. H.

Uric Acid in the Saliva in the Uric Acid Diathesis. By BOUCHERON (*Compt. rend. Soc. Biol.*, 1896, [x], 3, 454—456).—By the murexide test, uric acid can be detected in the saliva in patients suffering from the uric acid diathesis, particularly in the intervals between meals. An analogy is drawn between this and the occurrence of sugar in the urine in diabetes. W. D. H.

Toxicity of Aqueous Solutions of Phosphorus. By THOMAS BOKORNY (*Chem. Zeit.*, 1896, 20, 1022).—Phosphorus is a poison to low organisms, but not a powerful one. As with nitroglycerol, there is here a difference between low animals and plants and those higher in the scale. W. D. H.

Excretion of Water and Carbonic Anhydride from Inflamed Skin. By WAKELIN BARRATT (*J. physiol.*, 1897, 22, 206—214).—In dry dermatitis produced by carbolic acid, the output of water is much diminished (56 per cent.); this persists till desquamation is completed. No marked alteration is noted in the elimination of carbonic anhydride, until, when desquamation is in progress, the horny epithelium becomes thinner; there is then a tendency to increased output. W. D. H.

Glycosuria after Carbonic Oxide Poisoning. By WALTHER STRAUB (*Chem. Centr.*, 1896, ii, 1040; from *Arch. exp. Path. Pharm.*,

38, 139—157).—After poisoning dogs by carbonic oxide, sugar appears in the urine if proteid decomposition occurs; but in proteid hunger, or with excess of carbohydrate food, it is absent. Administration of gelatin will take the place of proteid in this connection.

W. D. H.

Nitroglycerol as a Poison. By THOMAS BOKORNY (*Chem. Zeit.*, 1896, 20, 1021—1022).—Nitroglycerol is a very feeble poison to low organisms, whilst nitroethane is not only non-poisonous to these, but appears to increase their nutrition.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nitrated Carbohydrates as Food Material for Moulds. By THOMAS BOKORNY (*Chem. Zeit.*, 1896, 20, 985—986).—Cellulose tri-nitrate (nitrocellulose) will serve as a food supply for moulds when suspended in distilled water containing the requisite mineral matter and placed in the dark. The growth is rapid, and a considerable quantity of the vegetable growth accumulates round the masses of cellulose nitrate, but no growth is observed if mineral matter is absent. Cellulose itself cannot act as a food supply, and it seems probable that if glycerol is present cellulose nitrate is no longer made use of.

J. J. S.

Fixation of Atmospheric Nitrogen by the Association of Algæ and Bacteria. By RAOUL BOUILHAC (*Compt. rend.*, 1896, 123, 828—830).—*Nostoc punctiforme* was cultivated in flasks containing (Nos. 1—6) nutritive solutions free from nitrogen, with and without soil bacteria. A second series of experiments was made (Nos. 7—18) in which potassium arsenate (As = 0·01 per cent.) was added to the nutritive solution. It had been previously shown that certain algæ are able to live in presence of arsenic. The following results were obtained.

No.		Dry produce (grams).	Nitrogen.	
			Total (grams).	Per cent. in dry subst.
1—3	without bacteria	—	—	—
4	with bacteria	0·705	0·0234	3·3
5	„ „	0·564	0·020	3·5
6	„ „ and <i>Hypheothrix</i>	0·353	0·0111	3·1
7—10	without „	—	—	—
11	with „	0·322	0·0105	3·2
12	„ „	0·295	0·0118	4·0
13	„ „	0·183	0·0065	3·5
14	„ „	?	?	?
15	„ „	0·154	0·0058	3·7
16	„ „ <i>Hypheothrix</i> and <i>Pleurococcus</i> ..	0·322	0·0107	3·3
17	„ „ „ „ <i>Ulothrix</i> ...	0·381	0·012	3·6
18	„ „ and „	0·545	0·0206	3·7

There was, therefore, fixation of nitrogen during the growth of algæ associated with bacteria, and the percentage of nitrogen in the

produce is comparable with that of the *Leguminosæ*. Like *Nostoc*, the bacteria are capable of living in presence of arsenic in the quantity employed.

Schizothrix lardacea and *Ulothrix flaccida* failed to develop in absence of combined nitrogen, both with and without soil bacteria.

N. H. J. M.

Action of Formaldehyde on Germination. By RICHARD WINDISCH (*Landw. Versuchs.-Stat.*, 1897, 49, 223—226).—Selected seeds (200 of each) of winter-wheat, rye, barley, and oats were allowed to germinate between thick Swedish filter paper, with distilled water alone, and in presence of different amounts of formaldehyde (0·02 to 0·40 per cent.). The experiments extended over 12—16 days. The weakest solution retarded, on the first day, the germination of barley, wheat, and rye, but was favourable to oats as compared with water alone. The 0·08 per cent. solution had a considerable retarding effect, especially in the case of rye and wheat, but less with barley; oats germinated normally. With 0·12 per cent. of formaldehyde, the wheat was mostly destroyed, whilst the germination of oats, although retarded, was otherwise normal. The following results show the average percentage of seeds of each kind which germinated under the influence of the solutions of different strengths. There were two experiments in each case.

Formaldehyde per cent.	0	0·02	0·04	0·08	0·12	0·20	0·40
Barley	96·5	95·5	97·5	89·0	47·0	none	none
Wheat	98·0	97·25	97·25	88·5	9·25	„	„
Oats	97·0	99·50	99·25	96·5	95·5	64·5	„
Rye	96·25	93·5	91·05	65·25	20·50	1·5	„

The results of the duplicate experiments given differed by less than 5 per cent.

N. H. J. M.

How is the High Percentage of Iron in the Ash of *Trapa natans* to be Explained? By GEORGE THOMS (*Landw. Versuchs.-Stat.*, 1897, 49, 165—171).—The nuts examined were obtained from a lake near Jacobstadt in Courland, and included (1) black nuts which had been at least a year in the mud at the bottom of the lake, and (2) fresh nuts still containing the kernels. The following analytical results were obtained.

	Dry matter (grams).	Ash (grams).	Insoluble in HCl (grams).	Fe ₂ O ₃ (grams).	In dry matter, ash per cent.	In ash, Fe ₂ O ₃ per cent.
Kernels of 6 fresh nuts	5·2846	0·1740	0·0007	0·0023	3·29	1·32
Shells „ „ „ „	5·9328	0·1896	0·0034	0·0025	3·20	1·34
Black nuts (2)	1·4692	0·1100	0·0082	0·0746	7·48	67·82

The comparatively small amount of iron in the fresh nuts indicate that iron has no physiological rôle. It is supposed that the porous tissues of the dead nuts which contain tannin, precipitate the iron present in the water which surrounds them, until the whole of the tannin is used up. This would account for the blackening of the nuts, and

also accords with the results of analyses of black oak found in the river near Riga. The wood contained: water, 8.02; ash in dry substance 1.22, and Fe_2O_3 (in the ash) 50.14 per cent. (compare E. von Gorup-Besanez, *Annalen*, 118, 220—227). N. H. J. M.

Sugar and Starch in Resting Potatoes. By WILHELM BERSCH (*Chem. Centr.*, 1896, ii, 1121; from *Österr.-ung. Zeit. Zucker.-Ind. u. Landw.*, 25, 766—793).—If potatoes are slowly frozen, or kept for a long time near their freezing point (-1°), some of the starch is changed into sugar, but if the freezing is done rapidly, no sugar can be detected; the sugar formed is chiefly dextrose, but partly cane-sugar. If they are again warmed, part of the sugar is used for respiratory purposes, and part is again transformed into starch. W. D. H.

Formation of Starch. By THOMAS BOKORNY (*Chem. Zeit.*, 1896, 20, 1005—1006).—In absence of organic matter, carbonic anhydride, light, and potash are necessary for the production of starch, whilst in presence of sugar or glycerol, &c., light is not essential (compare E. Laurent, "*Sur la formation d'amidon dans les plantes*," Brussels, 1888). This does not, however, hold good for all plants, as, for instance, *Spirogyra maxima*, which failed to produce starch in 48 hours in 1 per cent. sugar (cane-sugar, dextrose, and xylose). Moreover, *Spirogyra* could be freed from starch by keeping it 5—10 days in darkness; in 1 per cent. dextrose (both with 0.5 per cent. potassium nitrate and without potash); the dextrose did not even delay the disappearance of the starch. In presence of light, *Spirogyra* produced starch abundantly from cane-sugar, grape-sugar, and glycerol, &c., but not in an atmosphere of hydrogen.

Similar results were obtained with *Confervæ*. Whilst many plants, such as potatoes, convert sugar into starch in absence of light, it is still unknown whether the presence of oxygen is necessary or not.

N. H. J. M.

Formation of Non-nitrogenous Reserve Substances in Walnuts and Almonds. By LECLERC DU SABLON (*Compt. rend.*, 1896, 123, 1084—1806).—Walnuts and almonds were examined at different periods of growth, commencing in July and June respectively, when the embryo was only slightly developed. They were dried for 3 days at 45° ; glucose, saccharose, and the amyloses were determined. The following percentage results in dry matter are given, as well as the amount of water to 100 points of dry matter.

		Water.	Oil.	Glucose.	Saccharose.	Amyloses.
1. Walnuts,	6 July.....	837	3	7.6	0	21.8
„	1 Aug. ...	535	16	2.4	0.5	14.5
„	15 Aug. ...	274	42	0	0.6	3.2
„	1 Sept. ...	48	59	0	0.8	2.6
„	4 Oct.	10	62	0	1.6	2.6
2. Almonds,	9 June ...	896	2	6.0	6.7	21.6
„	4 July.....	716	10	4.2	4.9	14.1
„	1 Aug. ...	219	37	0	2.8	6.2
„	1 Sept. ...	117	44	0	2.6	5.4
„	4 Oct.	12	46	0	2.5	5.3

The amount of fatty acids was much greater during the earlier stages of development than later, owing to conversion into carbohydrates; glucose is also to be considered as an intermediate product. In almonds, there was decrease in the percentage amount of saccharose, but an increase in actual amount.

N. H. J. M.

Amount of Lecithin in some Seeds and Oil Cakes. By ERNST SCHULZE (*Landw. Versuchs.-Stat.*, 1897, 49, 203—214).—The following amounts of lecithin were found in various seeds and cakes (per cent. of dry matter).

Seeds: Blue and yellow lupins (without husks), 2.20 and 1.64; vetches, 1.09; peas, 1.05; lentils, 1.03; wheat, 0.43; barley, 0.47; maize 0.25; buckwheat, 0.53; flax, 0.73; hemp, 0.85; *Pinus sylvestris*, 0.49; *Picea excelsa*, 0.27; *Abies pectinata*, 0.11 (compare Stoklasa, Abstr., 1897, ii, 116).

Cakes: Earth-nut (1), 0.20; (2) 0.37; sesame, 0.49; linseed, 0.44; cocoanut, 0.30; cotton seed, 0.49. Maxwell (Abstr., 1891, 511) found 0.94 per cent. of lecithin in cotton-seed.

The above results can only be correct on the assumption that lecithin is the only compound, soluble in alcohol and ether, which contains phosphorus; this may safely be assumed in the cases under consideration, namely, seeds and oil cakes, but perhaps not in the case of chlorophyllous objects (Stoklasa, Abstr., 1897, ii, 116).

Lecithin isolated from wheat germs had all the properties of preparations from leguminous seeds.

Before extracting with ether and alcohol, seeds must be very finely ground. Seeds which contain much fat are first coarsely ground, extracted with ether, and then ground as finely as possible. Von Bitto (Abstr., 1894, ii, 402) recommended extraction with methylic alcohol. The author found, however, that the "purest methylic alcohol," from different sources, dissolved small amounts of potassium and sodium phosphates, and determinable amounts of phosphorus from seeds from which the whole of the lecithin had previously been extracted.

N. H. J. M.

A Phosphorus Compound from Plants, which yields Inosite on Decomposition. By ERNST WINTERSTEIN (*Ber.*, 1897, 30, 2299—2302).—The compound containing phosphorus in combination with calcium and magnesium, which was extracted from the seeds of *Sinapis nigra* by means of dilute sodium chloride solution, is now found to be most conveniently extracted by heating the dried seeds with dilute acetic acid; it is a white, earthy, amorphous mass, and after removal of the calcium by means of oxalic acid, yields a compound containing 42.24 per cent. P_2O_5 and 12.97 per cent. MgO . An attempt to obtain the free acid was unsuccessful, although on heating the magnesium salt in a closed tube with concentrated hydrochloric acid at 140° for 30 hours, inosite was formed.

J. F. T.

Lactic Acid in Algerian Wines. By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1896, [iii], 15, 1210—1213).—The author has analysed fourteen Algerian wines, the lactic and succinic acids being separately estimated by the method that he has described (this vol., ii, 57). The total solid

residue at 100° varied from 20·00 to 35·00 grams per litre, the total acidity, in terms of sulphuric acid, from 5·49 to 9·82, the lactic acid from 0·52 to 4·54, and the succinic acid from 0·66 to 1·60 grams per litre, whilst the alcoholic strength varied 9·85 to 13·00 per cent. by volume. The relative proportions of lactic acid and mannitol show that the greater part of the former has not been produced by a mannitol fermentation of glucose or levulose. The wines contain the vibrios found by Pasteur in "turned" wines, but differ from the latter in containing normal proportions of tartrates and of glycerol. All the wines, however, contain a notable proportion of glucose, and it seems most probable that the vibrios, before attacking the glycerol and the tartrates, convert a larger or smaller proportion of the glucose into lactic acid. The "turning" ferment is widely diffused, and the high temperatures that prevail in Algeria often prevent the completion of the alcoholic fermentation whilst favouring the development of the vibrios.

C. H. B.

Composition of Potatoes. By BALLAND (*Compt. rend.*, 1897, 125, 429—431).—Analyses of a large number of varieties of potatoes, grown in France, gave the following results.

		Nitrogen		Sugars		Ash.	Weight
		com-		and	Cellu-		
		Water.	pounds.	Fats.	starch.	lose.	of tubers.
Ordinary condition	{ Minimum	66·10	1·43	0·04	15·58	0·37	0·44
	{ Maximum	80·60	2·81	0·14	29·85	0·68	1·18
Dry	{ Minimum	0·0	5·98	0·18	80·28	1·40	1·66
	{ Maximum	0·0	13·24	0·56	89·78	3·06	4·38

The proportion of water is independent of the size of the tubers and of the variety of potato, but seems to be closely connected with the character of the soil; moreover, the proportion of nitrogen compounds varies considerably in different varieties. The ash generally contains traces of manganese. The acidity varies from 0·072 to 0·250 per cent. Young tubers do not differ from mature tubers in composition except that the envelope amounts to only about 3 per cent. and the proportion of cellulose is about seven times as great in the young as in the mature tubers. When cooked in water, potatoes alter very little in weight. Three kilograms of boiled, or about 1200 grams of fried potatoes contains almost exactly the same quantity of nitrogen compounds and starches as 1 kilogram of ordinary white bread.

C. H. B.

Banana Flour. By JOHN B. COPPOCK (*Chem. News*, 1897, 75, 265—266).—In some parts of Cuba, the fruit of *Musa paradisiaca*, a variety of banana, is the chief food of the natives; a sample of the flour had the following percentage composition: water, 10·62; proteids, 3·55; fat, 1·15; carbohydrates, 81·67; fibre, 1·15; phosphoric acid, 0·26; salts other than phosphates, 1·60. The flour has the appearance of finely-ground oatmeal, has an agreeable odour, and quickly forms a thin, readily digestible mucilage with warm water. The starch granules are elongated and elliptical, and consist of concentric layers.

D. A. L.

Composition of the Seeds of Mangel Wurzel. By ARTHUR DEVARDA (*Landw. Versuchs.-Stat.*, 1897, 49, 239—240).—The entire seeds (shell and kernel) of seven (mostly Austrian) varieties of mangel wurzel were analysed. The average percentage composition of the dry matter (88·45 per cent. in the fresh substance) was as follows:

N × 6·25.	Crude fat.	N-free extract.	Crude fibre.	Ash.
12·84	6·08	38·41	34·01	8·38

The pure ash contained (per cent.)

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
22·01	8·01	16·14	11·07	1·03	10·00	5·01	24·61	2·32

N. H. J. M.

Analytical Chemistry.

Sensitive Litmus Paper. By RONDE (*Chem. Centr.*, 1896. ii, 1130; from *Pharm. Zeit.*, 41, 736).—Coarsely powdered litmus is digested during one day with 12—15 parts of water, and the dark-blue mixture after being treated with concentrated sulphuric acid until the colour turns to bright red, is heated on a water bath to expel carbonic anhydride; dilute sulphuric acid is then added until filter paper dipped in the liquid just appears violet-red. When cold, the liquid is filtered, and by addition of more dilute sulphuric acid, or of powdered litmus, it is adjusted so as to give either a blue or a red stain to filter paper. M. J. S.

Application of Iodic Acid to the Analysis of Iodides. By FRANK A. GOOCH and C. F. WALKER (*Amer. J. Sci.*, 1897, [iv], 3, 293—300, and *Zeit. anorg. Chem.*, 14, 423—431).—The authors have worked out a new process for the estimation of iodides. An excess of solution of potassium iodate is first added, and then dilute sulphuric acid, which causes iodine to be set free; solution of potassium hydrogen carbonate is then added in slight excess, followed by a very slight excess of standard arsenious acid; finally, the undecomposed arsenious acid is titrated with standard iodine, using starch solution as indicator. The amount of iodine to be estimated is five-sixths of the iodine thus found.

To ensure success, the amount of iodide should be something like 0.08 gram dissolved in 150 c.c. of liquid. Small quantities of bromides or chlorides do not interfere with the process. L. DE K.

Detection of Fluorine in Silicates and Borates. By JULIUS A. REICH (*Chem. Zeit.*, 1896, 20, 985).—The substance is gently heated with a little strong sulphuric acid in a platinum crucible covered with a watch glass, which is placed with its convex side downwards, and is moistened with a drop of water. If fluorine is present, a coating of silicic or boric acid will soon be visible; the latter readily dissolves in a drop or two of water. L. DE K.

Estimation of Sulphur in Iron. By WILHELM SCHULTE (*Chem. Centr.*, 1896, ii, 1132; from *Stahl und Eisen*, 16, 865).—The iron (10 grams) is dissolved in 200 c.c. of hydrochloric acid (1 vol. of sp. gr. 1.19 diluted with 2 vols. of water), and the gases passed through 45–50 c.c. of a solution containing 5 grams of cadmium acetate, 20 grams of zinc acetate, and 200 c.c. of glacial acetic acid per litre; when the reaction is complete, and the absorbent solution is warmed to 30–40° by the escaping steam, 5–7 c.c. of copper sulphate solution (80 grams of crystallised copper sulphate and 320 grams of concentrated sulphuric acid per litre) is added, whereby the precipitated sulphides are immediately converted into copper sulphide. This is collected, washed with hot water, roasted, and then strongly ignited until converted into cupric oxide, from the weight of which the sulphur is calculated. Cupric acetate cannot be used for the original absorption, in consequence of the presence of hydrogen phosphide, by which some copper would be precipitated.
M. J. S.

Estimation of Total Ammonia in Gas-liquors. By EDUARD DONATH and K. POLLAK (*Zeit. angew. Chem.*, 1897, 555–557).—The authors have proved that the only trustworthy process for estimating ammonia in gas-liquors is the distillation method. The gas-volumetric process, consisting in liberating the nitrogen by means of bromine dissolved in aqueous soda, gives results which are decidedly too high. This is caused by a partial decomposition of the thiocyanates always present in the samples.
L. DE K.

Estimation of Nitric Acid by Electrolysis. By KARL ULSCH (*Zeit. Elektrochem.*, 1897, 3, 546–547).—The nitric acid is electrolytically reduced to ammonia, employing as the cathode a spiral of about forty turns of soft copper wire, about 1.4 mm. thick, wound on a glass tube of about 15 mm. diameter, the coil being afterwards stretched out to a length of about 70 mm.; before use, the copper spiral is heated to dull redness and quenched in water; a platinum wire, 1 mm. thick and 20 cm. long, is employed as the anode. These electrodes reach almost to the bottom of a test-tube, and are held in place by a rubber stopper, through which a glass tube passes to permit of the escape of gases; the current of 1.25 ampères (or 1.5 amp. per sq. dm.) employed is furnished by two accumulators in series. The nitrate is dissolved in semi-normal sulphuric acid. Until some 90 per cent. of the nitrate is reduced, no hydrogen is evolved, and 10 minutes after the first bubbles of hydrogen come off the reduction is completed. The results obtained with potassium nitrate are very accurate so long as at least two-fifths of the sulphuric acid originally present remains unneutralised, but unfortunately, many substances, especially chlorides, which accompany naturally occurring nitrates, are prejudicial to the accuracy of the method.
T. E.

Estimation of Nitrates in Soil. By L. KUNTZE (*Chem. Centr.*, 1896, ii, 1133; from *Zeit. Ver. Rubenzuck. Ind.*, 1896, 761).—An attempt to utilise the reaction with brucine and sulphuric acid as a quantitative one, by comparing the depth of colour produced by a single drop of the soil extract with that yielded by a drop of a standard

nitrate solution, failed to give constant results, the depth of colour varying both with the size of the drops and with the quantity of sulphuric acid added.

M. J. S.

Estimation of Nitrogen in Nitrated Guanos. By V. SCHENKE (*Chem. Zeit.*, 1896, 20, 1031—1033).—The author again states that the only method which gives satisfactory results with "nitrated guanos" is the one proposed by him in 1893, which he termed the Ulsch-Kjeldahl method.

In this process, the nitric nitrogen is first reduced by means of reduced iron and dilute sulphuric acid, and the whole is then boiled with sulphuric acid and a drop of mercury until the organic matter is destroyed. The ammonia is then determined as usual (*Abstr.*, 1894, ii, 67).

L. DE K.

Detection of Nitrites in Potable Water. By A. GAWALOWSKI (*Chem. Centr.*, 1896, ii, 1009; from *Zeit. Nahrungsm. Hyg. War.*, 10, 315).—The reaction with potassium iodide and starch is only trustworthy when the iodide is free from iodate, and has been preserved in the dry state and in the dark in bottles of yellow or blue glass; dilute hydrochloric acid should be used for acidifying, since dilute sulphuric acid is apt to be reduced by dust to sulphurous acid. It is necessary that the starch should be washed immediately before it is gelatinised, and that the starch-paste be freshly made.

M. J. S.

Analysis of Phosphor-bronze, Phosphor-copper, Phosphor-tin, &c. By MAX WICKHORST (*J. Amer. Chem. Soc.*, 1897, 19, 396—398).—*Estimation of Phosphorus alone.*—One gram of the sample is heated with a mixture of 15 c.c. of nitric and 5 c.c. of hydrochloric acid. When oxidised, the acid liquid is diluted, mixed with ammonia in excess, and the whole made up to 200 c.c.; hydrogen sulphide is then passed through the solution until the copper, lead, &c., are entirely precipitated. Ammonia and magnesium mixture are added to 100 c.c. of the filtered liquid, and after a few hours the magnesium phosphate is collected, washed with dilute ammonia containing a little ammonium sulphide, and weighed, as usual, as magnesium pyrophosphate.

Complete Analysis of Phosphor-bronze.—Half a gram of borings, treated with 5 c.c. of strong nitric acid until fully oxidised, is diluted with water and the insoluble matter collected on a filter and washed with dilute nitric acid. The filter and contents are then ignited in a weighed porcelain crucible, being gradually heated to redness; the weight is that of the stannic oxide *plus* phosphoric anhydride. After being fused with 0.5 gram of dry sodium carbonate and 1 gram of sulphur, with the cover on the crucible, until the excess of sulphur is volatilised, it is allowed to cool, and the fused mass dissolved in water; excess of ammonia and 1 gram of ammonium chloride are then added, and the phosphoric acid precipitated with magnesium mixture. The precipitate should be purified by redissolving it in a little hydrochloric acid and reprecipitating with ammonia, before finally weighing as magnesium pyrophosphate. From the latter, the phosphorus can be

calculated and also the corresponding amount of phosphoric anhydride ; the latter deducted from the weight of the stannic precipitate gives the stannic oxide, which is then calculated to tin. As, however, a little of the phosphoric acid passes into the original nitric acid filtrate, it is advisable to make a special duplicate experiment in which the phosphoric acid in the filtrate can be estimated by the molybdic process.

To the acid filtrate, after it is neutralised with ammonia, 5 c.c. of nitric acid is added, the whole diluted to 150 c.c., introduced into a large platinum dish, and electrolysed, the lead being precipitated as dioxide on the dish and the copper on the negative electrode, which consists of a piece of platinum foil 2 inches square. The liquid contains any iron or zinc which may be present ; these are precipitated as sulphides by adding ammonia and ammonium sulphide, and the precipitate, after being collected and ignited in a porcelain crucible, is weighed ; the mixed iron and zinc oxides are dissolved in hydrochloric acid and the ferric oxide precipitated with ammonia, the zinc oxide being found by difference.

L. DE K.

Estimation of Phosphoric Acid in Potable Waters. By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1896, [iii], 15, 1213—1217).—The estimation of phosphoric acid in potable waters by weighing the ammonium phosphomolybdate is inexact, because the solubility of the precipitate in dilute nitric acid introduces errors of the same order of magnitude as the quantities to be determined.

The author finds (1) that at equal temperatures the intensity of the yellow colour of the liquid after addition of the molybdate is directly proportional to the quantity of phosphoric acid present, at any rate up to 0.03 gram per litre, and (2) the intensity of the coloration increases with the temperature, and between 10° and 30° is directly proportional to the temperature, the increase in intensity with rise of temperature being represented by straight lines.

Solutions of potassium chromate form a convenient colour scale, but a scale can also be made by means of dilute solutions of a phosphate, 50 c.c. of which is mixed with 2 c.c. of a molybdate solution prepared by dissolving 150 grams of ammonium molybdate in 1000 c.c. of water, and pouring this solution into 1000 c.c. of nitric acid of sp. gr. 1.2. The tubes are well corked, and the corks covered with paraffin ; the solutions remain unaltered for two or three months, but those containing more than 0.010 gram of phosphoric acid per litre gradually deposit a precipitate after that time. When kept at 40° for several days, no precipitate forms even in the solutions that contain 0.025 gram of phosphoric acid per litre.

A litre of the water is evaporated after addition of nitric acid, and the residue is repeatedly evaporated with nitric acid to separate all the silica ; it is then dissolved in 50 c.c. of nitric acid, mixed with 2 c.c. of the molybdate solution, and the intensity of the yellow coloration compared with the scale of units.

The presence of silica introduces an error, but the coloration due to phosphoric acid reaches its maximum intensity almost instantaneously, whereas with silica the intensity increases slowly. Observations made

after sufficient intervals of time will show whether the intensity is increasing or is constant.

C. H. B.

Solubility of Phosphates in Citric Acid and Ammonium Citrate. By OTTO FOERSTER (*Chem. Zeit.*, 1897, 20, 1020—1021).—The author's experiments prove that there is yet a good deal to be investigated before the citrate-solubility controversy is finally settled.

It appears that this solubility is greatly influenced by the amount of soluble silica. Another strange thing is that some phosphates were found to be more soluble in Wagner's ammonium citrate solution than in a 1.4 per cent. solution of citric acid, whilst the majority of phosphates are more readily soluble in the latter.

L. DE K.

Arsenical Sulphuric Acid, a Source of Error in Naumann's Process for Estimating Phosphoric Acid. By GUSTAV LOGES and KARL MÜHLE (*Chem. Zeit.*, 1896, 20, 984).—In Naumann's process for estimating phosphates soluble in citric solution, the citric acid solution of the basic slags is boiled with sulphuric and nitric acids until the organic matter is destroyed. The phosphoric acid is then estimated by the magnesia or molybdate method.

If there is any arsenic present in the sulphuric acid employed, this will be oxidised to arsenic acid, and will then be precipitated along with the phosphoric acid. The use of a pure acid is therefore indispensable.

L. DE K.

Estimation of Boric Acid in Foods. By LEONARD DE KONINGH (*J. Amer. Chem. Soc.*, 1897, 19, 385—388).—When using Thomson's process for estimating boric acid, it is necessary to completely expel by boiling any carbonic anhydride that may be present; the author states that there is no fear of loss of boric acid, even if the boiling is continued for 15 minutes, which is far longer than is necessary.

When dealing with articles of food, the presence of phosphoric acid has to be taken into account; a process of separating it by means of calcium chloride is given, differing greatly in detail from that previously published by Thomson. A new process is also described by which the boric acid can be estimated after removal of the phosphoric acid by means of magnesium mixture; the filtrate is mixed with excess of sodium carbonate and heated, the precipitate of magnesia is removed by filtration, the filtrate evaporated to dryness to render the rest of the magnesia insoluble, and the residue is then treated with a little water and filtered. The boric acid can be titrated according to Thomson's directions. As a test experiment, 0.1 gram of boric acid was dissolved in aqueous soda, and mixed with 100 grams of oatmeal and incinerated; from the ash, 0.095 gram of boric acid was recovered.

L. DE K.

Estimation of Silica in Blast-furnace Slag. By G. H. MEEKER (*J. Amer. Chem. Soc.*, 1897, 19, 370—374).—The author recommends the following process, which is particularly suitable if the sample contains an admixture of spinel. 0.5 gram of the finely ground slag is placed in a small dish, moistened with 3 c.c. of water, 10 c.c. of hydrochloric acid added, and the whole well stirred. When the slag has nearly all dissolved, 40 c.c. of dilute sulphuric acid (1 : 1) is added, and

the mixture boiled until fumes of sulphuric acid are given off. When cold, a little water and 10 c.c. of hydrochloric acid are added, and the whole is boiled for a minute. The insoluble matter, consisting of nearly chemically pure silica, is collected on a filter, and after being washed with hot dilute hydrochloric acid and then with water, is ignited and weighed.

L. DE K.

Separation of Silicic and Tungstic Acids. By JAMES S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, 1897, 19, 377—379).—The author confirms the statement that tungstic acid cannot be accurately separated from silica by means of ammonia, as the latter is also sensibly soluble in that liquid; the solubility is certainly diminished if it has been strongly ignited, but in that case the tungstic acid also becomes less readily soluble.

The best plan is to first weigh the mixed oxides, then to remove the silica by evaporating with hydrofluoric and sulphuric acids, and weigh the residue of tungstic acid.

L. DE K.

Estimation of Potash and Phosphoric Acid in Fodders. By HARVEY W. WILEY (*J. Amer. Chem. Soc.*, 1897, 19, 320—322).—This is a slight modification of the Lindo-Gladding process for estimating potash, and admits of the determination of the phosphoric acid in the same portion of the sample.

Eight grams of the substance is burnt as completely as possible over a small flame, the ash is dissolved in 50 c.c. of water mixed with 5 c.c. of hydrochloric acid, and transferred to a 200 c.c. measuring flask. Some ferric chloride is added to precipitate the phosphoric acid, and then 10 c.c. of strong ammonia and 10 c.c. of a 20 per cent. solution of ammonium carbonate. After heating on the water bath for an hour, the liquid is left over-night, made up to the mark, thoroughly shaken, and poured on to a large filter; when this is drained and has become somewhat dried, it is put back into the flask. Dilute nitric acid is added to dissolve the ferric phosphate, the solution is made up to a definite bulk, and an aliquot part is used for the estimation of the phosphoric acid.

Fifty c.c. of the filtrate containing the potassium is then evaporated to dryness in a platinum dish, the bulk of the ammonium chloride expelled by heating, and the residue, after being moistened with 1 c.c. of dilute sulphuric acid (1:1), is again gradually heated to redness. The potassium is then estimated by means of platinic chloride by the Lindo-Gladding method. The washing with alcohol, solution of ammonium chloride, and the final washing with alcohol are best done in a Gooch crucible. After weighing the double chloride, the contents of the crucible are dissolved in boiling water, and the crucible is dried and re-weighed.

L. DE K.

Electrolytic Estimation of Cadmium. By S. AVERY and BENTON DALES (*J. Amer. Chem. Soc.*, 1897, 19, 379—382).—The authors, having in view the excellent results obtained when electrolysing zinc from a formate solution, have applied the same process to cadmium with great success.

About 0.1 gram of cadmium is dissolved in dilute sulphuric acid, 6 c.c. of formic acid of sp. gr. 1.2 is added, and then solution of potassium carbonate until a slight turbidity is produced. This is removed by a little more formic acid; finally 1 c.c. more of this acid is added, and the mixture is diluted to 150 c.c. and submitted to electrolysis.

L. DE K.

Distribution of the Precious Metals and Impurities in Copper, and Suggestions for a Rational Mode of Sampling. By EDWARD KELLER (*J. Amer. Chem. Soc.*, 1897, 19, 243—258).—In order to get a fair sample of unrefined copper, plates from 8 to 10 inches square and 1 inch thick should be cast, and from these drillings should be taken at least 1 inch from the edge through the entire plate.

The author believes that when, on the solidification of a metal, the small amounts of impurities segregate or liquefy, and consequently concentrate towards the centre, the degree of concentration is greatest for those whose atomic volumes show the greatest difference as compared with that of the metal in which these impurities are present.

L. DE K.

Quantitative Electrolysis of Heavy Metals. By L. WOLMAN (*Zeit. Elektrochem.*, 1897, 3, 537—545).—The author gives the results of comparative trials of the principal electrolytic methods which have been proposed for the determination of the heavy metals.

Copper.—The best results are obtained with solutions in dilute sulphuric or nitric acid. Solutions containing ammonium oxalate require more time and attention, and from ammoniacal solutions the metal is apt to separate in the spongy condition.

Silver is easily precipitated at 50° from solutions containing 2 to 3 per cent. by volume of nitric acid (sp. gr. 1.36) or from solutions containing potassium cyanide.

Lead is best determined at 50° in solutions containing about 20 per cent. by volume of nitric acid (sp. gr. 1.36). The peroxide precipitate must be dried at 180—190°.

Manganese.—Fairly good results are obtained with solutions containing 1 to 1.5 per cent. by volume of strong nitric acid, using a very small current and warming to 50°. Solutions in potassium oxalate, acetic acid or ammonium pyrophosphate do not give satisfactory deposits.

Zinc is best deposited from strongly alkaline solution at 50° by means of a fairly strong current. Potassium or ammonium oxalate solutions are also satisfactory, but acetic or citric acids, ammonium acetate, potassium cyanide, or ammonium pyrophosphate are unsatisfactory.

Cobalt and nickel are best deposited from ammoniacal solutions; Classen's ammonium oxalate and Brand's ammonium pyrophosphate methods give good deposits, but somewhat high numbers.

Iron is deposited slowly but completely from solutions in ammonium oxalate.

Copper may be separated from zinc or nickel by first depositing the copper from an acid solution.

Zinc and nickel are separated by first depositing the zinc from an

alkaline solution containing Rochelle salt. If the electrolysis is too long continued, the zinc is apt to contain nickel.

Zinc and cadmium are separated accurately by precipitating the latter at 50° with a feeble current from a solution containing 1 or 2 per cent. by volume of dilute sulphuric acid.

Lead is separated from zinc, copper, or silver by precipitating it at the anode from a solution strongly acidified with nitric acid. In the case of silver, however, the lead peroxide contains some silver, and the silver deposit simultaneously formed at the cathode is spongy. Copper is not completely precipitated from the strongly acid solution.

Copper and silver are separated by employing an E. M. F. lower than that required to deposit copper, namely, 1.3 to 1.5 volts. The process is slow, so that it is easier to precipitate the silver as chloride.

T. E.

Detection and Estimation of Traces of Lead in Waters. By J. C. BERNTRUP (*Chem. Zeit.*, 1896, 1020).—The author has found that lead phosphate is absolutely insoluble in water containing free sodium phosphate, and utilises this fact for the detection and estimation of lead in drinking waters.

A few litres of the sample is, if necessary, rendered somewhat hard by adding calcium chloride, and excess of sodium phosphate is then added. The precipitate which forms during 24 hours contains all the lead. It is collected on a filter, and after being dissolved in nitric acid, the lead is recovered from the solution and identified by the usual methods.

L. DE K.

Estimation of Lead in Lead Ores. By RICHARD K. MEADE (*J. Amer. Chem. Soc.*, 1897, 19, 374—377).—The author recommends the following process. About 1 gram of the sample is treated in a platinum dish with 50 c.c. of a mixture of concentrated sulphuric and nitric acids (1 : 3). The dish is covered and heated on a sand-bath until the action of the acid has ceased. The cover is then removed, rinsed into the dish, and 15 c.c. of hydrofluoric acid added, the dish being heated until fumes of sulphuric acid begin to make their appearance. When cold, the residue is diluted to about 100 c.c., and the undissolved lead sulphate is collected and washed first with a 2 per cent. solution of sulphuric acid and then with alcohol. The precipitate is detached from the filter and ignited, the paper being burnt separately in the usual way.

If a sample of galena should contain calcite, this may be removed by a preliminary treatment of the ore with dilute hydrochloric acid, but it is always advisable to wash the lead sulphate thoroughly with acidified water in order to remove the last traces of calcium sulphate.

L. DE K.

Volumetric Estimation of Lead. By J. HOWARD WAINWRIGHT (*J. Amer. Chem. Soc.*, 1897, 19, 389—393).—The author recommends a process differing but slightly from that given in Crookes' "Select Methods." To estimate the amount of metallic lead in litharge, 1 gram of the sample is dissolved in 10 c.c. of nitric acid (sp. gr. 1.20), the solution is neutralised with excess of ammonia, and a large excess of

acetic acid is added ; the liquid is then heated to boiling and a solution of potassium dichromate run in from a delicate burette until the bulk of the lead has been precipitated. The dichromate solution should be made of such a strength that 1 c.c. represents a quantity of lead not greatly differing from 0.01 gram. The solution is now again boiled until the lead chromate has become orange coloured, and the titration is then cautiously continued until the precipitate settles promptly. The dichromate is now added a drop at the time, until a few drops of the supernatant liquid put on to a white porcelain tile gives a distinct red coloration with a drop of a 2 per cent. solution of silver nitrate.

Other metals which are precipitated by potassium dichromate or which exercise a reducing action on it should be first removed. Red lead should be dissolved in dilute nitric acid with the addition of oxalic acid ; white lead may be at once dissolved in acetic acid.

L. DE K.

Sodium Peroxide as a Third [Iron-zinc] Group Reagent.—By SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1897, 19, 341—348).—The metals of this group may be, to some extent, separated by means of aqueous potash or soda ; but in the presence of chromium, the separation is far from complete, as this metal is partly retained by the precipitate, particularly in the presence of zinc.

The author recommends dissolving the ammonium sulphide precipitate in nitric acid, and after neutralising with soda, heating the solution with excess of sodium peroxide. The chromium will then be converted into sodium chromate, and the other metals, except zinc and aluminium, will be left insoluble as hydroxides, or peroxides ; they are usually free from phosphoric acid.

L. DE K.

Estimation of Manganese in Iron Ores in the Dry Way. By BÜTTGENBACH (*Chem. Centr.*, 1896, ii, 1134 ; from *Rev. Univers. ; Berg.-Hüttenm.-Zeit.*, 55, 368).—Two fusions are made ; the one with an acid flux, the other with a basic flux. The regulus of the former contains only the iron of the ore, the slag containing the manganese as silicate. The regulus of the latter contains the iron with the reducible manganese, and its excess of weight over the former should agree with the excess of weight found in the slag of the acid fusion (allowing for the oxygen required to form manganous oxide). Should they not agree, the difference is due to the non-reduction of part of the manganese in the ore, in consequence of a deficiency in the amount of iron present. Ores rich in manganese can be smelted without the addition of lime ; the regulus then contains the iron free from manganese and containing only traces of carbon.

M. J. S.

Estimation of Manganese by Electrolysis. By CARL ENGELS (*Zeit. Elektrochem.*, 1897, 3, 286—289, and 305—308).—Further details are given of the method previously described (*Abstr.*, 1896, ii, 276), of determining manganese by depositing it electrolytically as peroxide from solutions containing chrome alum, or alcohol and ammonium acetate.

Manganates and permanganates are first reduced by a small excess of hydrogen peroxide in acetic acid solution, the hydrogen peroxide

destroyed by a little chromic acid, the ammonium acetate and chrome alum added, and the free acetic acid neutralised by ammonia; the solution is then electrolysed in an etched platinum basin at about 80° , and the adherent deposit thus obtained is heated for 3 or 4 minutes to redness to convert it into Mn_3O_4 . With 0.4 gram of manganese in 150 c.c. of solution containing 2 grams of chrome alum and 10 grams of ammonium acetate, the precipitation is complete in about $1\frac{1}{4}$ hours with a current density of 0.8 to 1 ampère per sq. dcm. The results of the test analyses given are excellent.

Heavy metals must first be removed when they occur along with manganese, and when the filtrate from them is dilute or contains substances which would interfere with the electrolytic separation, the manganese is best precipitated with hydrogen peroxide and ammonia, and then redissolved and treated as above described.

The determinations can be made with smaller currents, but the time required is correspondingly longer. At ordinary temperatures, 1.25 volts and at 80° 1.1 volts are sufficient to produce decomposition, but in the cold the precipitation is complete only after a very prolonged action of the current, and the precipitate is brittle and does not adhere well to the dish. In order to obtain a sufficiently adhesive precipitate, the electrolysis must be conducted at 80° and in presence of chrome alum; the latter may be replaced by alcohol, though this is less certain in its results, and requires the application of at least 2 volts. The reason of the variations in the properties of the precipitate is discussed at length; the author considers that MnO_2 and Mn_2O_3 are the primary products of the electrolysis, and that they are deposited as a brittle, metal-like coating. If, however, oxygen is simultaneously separated at the anode, it is supposed to act, in the nascent state, as a reducing agent, rendering the coating porous and not brittle. The chrome alum acts partly by reducing the manganese peroxide, partly by taking up some of the oxygen and so modifying the evolution of gas that the coating is not mechanically disturbed. The inferior results obtained with alcohol are due to the fact that it merely acts in the second way and not in the first.

With a current density of 0.8 to 1 ampère per sq. decimetre and with 0.2 to 0.3 gram of manganese, the quantity of chrome alum employed may be varied from 1 to 3 grams; with larger or smaller quantities, the deposit of manganese peroxide is brittle and non-adhesive.

T. E.

Estimation of Iron in Limestones. By DÉsirÉ DE PAEPE (*Chem. Zeit.*, 1896, 20, 1004).—5 to 10 grams of the sample is boiled for 5 minutes with strong hydrochloric acid, some water added, and the liquid filtered; after the addition of nitric acid, the mixture is boiled, and the iron and alumina are precipitated by ammonia, collected on a filter, and washed. The filtrate is made up to a definite volume, and may then be used for the estimation of lime, magnesia, alkalis, &c. The ferric precipitate is dissolved in hydrochloric acid, diluted to 125 c.c., and an aliquot portion mixed with excess of tartaric acid; the iron is then precipitated with ammonia and ammonium sulphide, the precipitate being finally converted into ferric oxide. L. DE K.

Qualitative Separations with Sodium Nitrite in Absence of Phosphates. By GILLET WYNKOOP (*J. Amer. Chem. Soc.*, 1897, 19, 434—436).—The author states that iron, chromium, and aluminium may be completely separated from zinc, manganese, cobalt and nickel by adding to the solution, if necessary, a few drops of hydrochloric acid and then boiling with excess of sodium nitrite. It is advisable to first reduce the iron to the ferrous state, as it then gives a more granular precipitate.

The author's test experiments, although only qualitative, are perfectly satisfactory. L. DE K.

Electrolytic Separation of Nickel and Cobalt from Iron. By O. DUCRU (*Compt. rend.*, 1897, 125, 436—439).—When a solution containing a ferric and a nickel salt is precipitated with excess of ammonia, part of the nickel is precipitated and part remains in solution, but if an electric current is passed through the liquid in which the precipitate is suspended, the whole of the nickel is deposited on the cathode. A very small quantity of iron is deposited at the same time, and a correction must be made by dissolving the metal and precipitating the iron after peroxidation; for practical purposes, however, the correction, which is always small, is rarely necessary.

The metal is dissolved, the solution evaporated to dryness with a slight excess of sulphuric acid, the residue dissolved in water, mixed with 5 to 10 grams of ammonium sulphate, heated, placed in the electrolysis apparatus, mixed with excess of concentrated ammonia, and subjected to the action of a current of 1·5 to 2·5 amperes for about 4 hours. The results quoted in the paper indicate that the method is very accurate.

In the case of steels, 0·25 to 0·30 gram is dissolved in aqua regia, evaporated with sulphuric acid, and treated as above.

It is not necessary to separate the silicon and carbon, and traces of manganese, chromium, and phosphorus do not affect the accuracy of the estimation. Traces of manganese are almost always deposited with the small quantity of iron, but the error due to this cause is negligible.

The author notes that a small portion of the metal deposited is insoluble in hydrochloric acid, but dissolves in aqua regia, and the latter solution gives the reactions of ferric salts.

Small quantities of chromic acid prevent the precipitation of the nickel by electrolysis from the ammoniacal solutions. C. H. B.

Estimation of Molybdenum Iodometrically. By FRANK A. GOOCH (*Amer. J. Sci.*, 1897, [iii], 237—240, and *Zeit. anorg. Chem.*, 14, 317—322).—The author defends his process (*Abstr.*, 1897, ii, 76) against the criticisms of Friedheim and Euler, and states that the results they obtained are vitiated by serious arithmetical errors.

L. DE K.

Analysis of Commercial Calcium Carbide and Acetylene, and Purification of the Latter. By GEORG LUNGE and EDWARD CEDERCREUTZ (*Zeit. angew. Chem.*, 1897, 651—655).—The authors point out the great difficulty there is in obtaining a thoroughly re-

presentative sample on account of the impossibility of obtaining a fine powder without moisture being absorbed and acetylene given off. About 50—100 grams of pea-sized lumps must therefore be taken for analysis; these are placed in a generating flask and brine is slowly added through a tap funnel until effervescence ceases; the gas is collected in a large gasometer over brine, or, better still, over water previously saturated with the gas. One hundred grams of chemically pure calcium carbide should yield 34.877 litres of gas at normal temperature and pressure.

Frequently the sample contains phosphorus, which is evolved as hydrogen phosphide, and sulphur which is partially given off as hydrogen sulphide and volatile sulphur compounds. To estimate these, 50—70 grams of the sample is treated as directed above, and the gases allowed to pass through a ten-bulb absorption tube filled with 75 c.c. of a 3 per cent. solution of sodium hypochlorite. This oxidises the phosphorus and sulphur to the corresponding acids; after precipitating the first with ammoniacal magnesium chloride, the second may be precipitated in the filtrate by adding hydrochloric acid and barium chloride.

Commercial acetylene may be purified by passing it first through a milk of chloride of lime, or, better still, over moist lumps of that substance. This treatment fully removes phosphorus and sulphur compounds. It may then be both dried and freed from ammonia by passing it through sulphuric acid of 1.6 sp. gr. L. DE K.

Estimation of Cyanogen by Silver Nitrate, using Potassium Iodide and Ammonia as Indicators. By WILLIAM J. SHARWOOD (*J. Amer. Chem. Soc.*, 1897, 19, 400—434).—The author, after criticising the various processes in use, recommends the following scheme. To the solution containing the cyanogen, 5 c.c. of ammonia and 2 c.c. of a 5 per cent. solution of potassium iodide are added, and then standard solution of silver nitrate until a faint, permanent cloudiness is produced. If the solution contains sulphides in small amount, 5—10 c.c. of a solution made by dissolving 0.5 gram of iodine and 2 grams of potassium iodide in 100 c.c. of water is used in place of the potassium iodide, but a special check should be made in such case. If the amount of sulphide is large, it must be removed by means of a solution of sodium plumbite; an aliquot part of the filtrate is then titrated.

If zinc is present, a large excess of alkali should be added; in this case, the cyanogen found represents, not only the potassium cyanide, but also the double zinc compound. By estimating the zinc, the amount of free potassium cyanide may be readily calculated, as 1 part of zinc corresponds with 4 parts of potassium cyanide. A similar allowance must be made if small quantities of copper are present. If calcium, magnesium, or manganese are present, ammonium chloride must be added, whilst soda is used in presence of aluminium or lead.

For technical purposes, it is best to prepare a silver nitrate solution containing 1.305 grams of this salt per 100 c.c.; taking samples of 10 c.c. each, 1 c.c. of the silver represents 0.1 per cent. of potassium cyanide. L. DE K.

Detection of Rhodinol in Ethereal Oils. By HUGO ERDMANN and P. HUTH (*J. pr. Chem.*, [ii], 56, 27—42). See this vol., i, 36.

Recalculation of Wein's Table for Starch Estimation. By WILLIAM H. KRUG (*J. Amer. Chem. Soc.*, 1897, 19, 452—454).—Wein has constructed a very useful table for calculating the amount of starch or dextrin from the amount of metallic copper obtained when employing Allihn's process for the estimation of starch. This table is based on the factor 0.90. There being some slight difference of opinion regarding the true molecular formula of starch, Ost states that the factor 0.925 should have been employed.

The author has, therefore, recalculated the table, using the average factor 0.92. L. DE K.

Estimation of Carbohydrates in Food-stuffs. By WINTHROP E. STONE (*J. Amer. Soc.*, 1897, 19, 183—197; 347—349).—The author has worked out a scheme for the estimation of carbohydrates in food-stuffs, as the methods generally employed are becoming obsolete, and do not satisfy the present demands.

In the author's process, the sample is finely ground or grated, and from 50 to 100 grams is first extracted, preferably in a Soxhlet apparatus, with 500 c.c. of strong alcohol to dissolve out any sugars; the residue is then exhausted with 500 c.c. of cold water to remove dextrin and soluble starch, and the undissolved part is air-dried. Two grams of the latter is boiled with 100 c.c. of water for half an hour, and, after cooling to 65°, it is digested with diastase at this temperature, in order to hydrolyse the starch. The residue left after this treatment is then boiled in a reflux apparatus with 100 c.c. of water and 2 c.c. of hydrochloric acid, to convert the gums, pentosans, hemicelluloses, &c., into reducing sugars; finally, the residue is boiled with aqueous soda (1.25 per cent.), and the crude fibre which is left is dried and weighed. L. DE K.

Improvements on Squibb's Volumetric Method for Estimating Acetone. By LYMAN F. KEBLER (*J. Amer. Chem. Soc.*, 1897, 19, 316—320).—The process differs from the original method (*Abstr.*, 1897, ii, 466) in so far that the use of pure acetone and the drop end-reaction are dispensed with. The following solutions are required: 1. A 6 per cent. solution of hydrochloric acid. 2. A decinormal solution of sodium thiosulphate. 3. An alkaline solution of potassium iodide made by dissolving 250 grams of the pure salt, making the liquid up to 1 litre, and adding 800 c.c. of aqueous soda containing 257 grams of soda per litre. 4. An approximately four-fifths normal solution of sodium hypochlorite, made by mixing 100 grams of 35 per cent. chloride of lime with 400 c.c. of water, and adding a solution of 120 grams of soda crystals in 400 c.c. of hot water; when cold, the clear liquid is decanted, diluted to 1 litre, and mixed with 25 c.c. of aqueous soda of sp. gr. 1.29. 5. A starch solution made by rubbing 0.125 gram of starch with 5 c.c. of cold water and then adding 20 c.c. of boiling water and again boiling for a few minutes; when cold, 2 grams of sodium hydrogen carbonate is added. The sample of acetone to be tested should be diluted with water to 50 or 100 times its weight. Twenty c.c. of the solution 3

is put into a stoppered flask, 10 c.c. of the acetone solution is added, and excess of solution 4 run in from a burette. After thoroughly shaking, the mixture is rendered acid by adding solution 1, excess of solution 2 is run in, and after a few minutes a little of solution 5 is added and the excess of thiosulphate re-titrated.

A blank experiment without the acetone having been made, the percentage of the latter can be readily calculated by remembering that 1 mol. of acetone requires 3 mols. of free iodine to form iodoform.

L. DE K.

Estimation of all the Volatile Fatty Acids in Butter. By EDUARD WRANPELMEYER (*Landw. Versuchs.-Stat.*, 1897, **49**, 215—218).—The filtered fat (about 5 grams) is heated in a 700—800 c.c. flask with 20 c.c. of glycerol sodium hydroxide (prepared by dissolving 100 grams of caustic soda in 100 c.c. of water and mixing 20 c.c. of the solution with 180 c.c. of glycerol) over a flame until frothing ceases and the liquid is clear. 250 c.c. of hot, boiled distilled water is carefully added, then a drop of indicator (litmus), and finally 50 c.c. of dilute sulphuric acid (20 c.c. of acid sp. gr. = 1.84 to 1 litre). The flask is immediately closed with a double bored cork fitted with a bulb-tube connected with a condenser at least 0.5 metre long, and a second tube for steam distillation. For the production of steam, boiled distilled water is employed, and the steam is passed through a connecting tube of copper (30 cm. long and 1.4 cm. wide) which is well heated with a flat burner. The distillation of 1.5 litres (collected in two portions of 1 and 0.5 litre) takes about an hour and a half. The distillate is filtered and half in each case (500 c.c. and 250 c.c. respectively) titrated.

All the water used in the process must be previously boiled to remove carbonic anhydride. In order to avoid any substance being mechanically carried over in the distillation, the bulb of the distilling tube must have a bent tube at the upper opening. Check experiments must be made with each apparatus, and potash must not be substituted for soda.

N. H. J. M.

Estimation of Lactic and Succinic Acids in Wines. By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1203—1206).—The succinic and lactic acids in wines are usually estimated together and expressed in terms of the equivalent quantity of sulphuric acid, but they can readily be separated by taking advantage of the fact that barium succinate is almost completely insoluble in alcohol of 80—83°, whereas barium lactate dissolves. The wine is mixed with quartz sand, evaporated to dryness under low pressure, and the residue dried over potash. It is then extracted with ether, the ether distilled off or allowed to evaporate spontaneously, the residue dissolved in water and the hot solution titrated with carefully purified barium hydroxide solution, using phenolphthalein as indicator. The neutral liquid is evaporated to dryness, mixed with 5 c.c. of warm water and 25 c.c. of absolute alcohol, and allowed to remain for several hours, after which it is filtered, the residue washed with alcohol of 80°, and the barium estimated in both the residue and the solution. Experiments made with liquids of known composition indicate that the results are too

low in the case of both acids, the error being greater in the case of the lactic acid, by reason of its volatility (compare this vol., i, 9).

C. H. B.

Estimation of the Acidity of Milk. By ARTHUR DEVARDA (*Chem. Centr.*, 1896, ii, 1003; from *Österr. Molkerei-Zeit.*, 1896, Sept.).—The author uses a stoppered flask holding 100 c.c. to the bottom of the neck, and with a cylindrical neck of 6 c.c. capacity graduated in half cubic centimetres. One hundred c.c. of milk, together with the necessary amount of 4 per cent. alcoholic phenolphthalein solution, reach to the zero mark, and when sufficient N/10 alkali has been added to produce the red colour, the reading on the neck gives at once the degree of acidity; 5 c.c. of alkali corresponds with 1 Soxhlet degree.

M. J. S.

Detection of Filicic Acid in Cases of Poisoning by Fern Extract. By ICARO BOCCHI (*Chem. Centr.*, 1896, ii, 1137; from *Boll. Chim. Farm.*, 1896, 20, 609).—The viscera are cut up, dried on the water bath, and extracted with a mixture of 1 part of absolute alcohol and 3 parts of ether; the extract is then evaporated, the greenish-brown residue treated with lime-water until a colourless solution is obtained, and the filtered solution acidified with acetic acid and shaken with carbon bisulphide. The residue from the bisulphide solution may be further purified by dissolving it in ether, and treating the solution with lime-water or neutral cupric acetate; the usual tests for filicic acid can then be applied. Filicic acid does not pass into the urine, but is decomposed in the organism.

M. J. S.

Analysis of Linseed Oil and Linseed Oil Varnish. By WALTHER LIPPERT (*Zeit. angew. Chem.*, 1897, 655—657. Compare *Abstr.*, 1897, ii, 529).—A criticism of Amsel's so-called water test for ascertaining the presence of rosin and rosin oil in linseed oil. This test consists in saponifying the sample with alcoholic potash and then adding water, when in the presence of adulterants a more or less decided turbidity will be noticed.

The author proves the test to be utterly untrustworthy.

L. DE K.

Examination of Resins. By KARL DIETERICH (*Chem. Centr.*, 1896, ii, 1137—1139; from *Ber. deut. pharm. Ges.*, 6, 247).—*Peru balsam*.—To obtain the saponification number, 1 gram is digested in the cold for 24 hours with 50 c.c. of light petroleum and 50 c.c. of N/2 alcoholic potash; 300 c.c. of water is then added and the liquid titrated with acid. The normal value is 260—270. For ascertaining the acid number, a dilution of 1:200 is necessary. Phenolphthalein should be added repeatedly and the titration continued until the supernatant liquid shows a distinct red colour after the brown, flocculent precipitate has subsided; values of 68—80 are obtained, whilst adulterations raise the acid number and lower the saponification number. The ether number, obtained by subtracting the acid number from the saponification number, varied only from 188 to 196 in the specimens examined by the author. Commercial samples contain 1.5—3 per cent. insoluble in ether. The ethereal solution serves for the estimation

of the cinnamein and the resin salts (peruresinotannol cinnamate), for which purpose it is shaken with 20 c.c. of a 2 per cent. solution of sodium hydroxide, and the two liquids carefully separated. Evaporation of the ethereal solution gives the cinnamein, and precipitation of the alkaline solution with hydrochloric acid the resin. The former should amount to 65—75 per cent., and the latter to 20—28 per cent. of the balsam.

Gum Ammoniacum.—The acid number is obtained by distilling 0.5 gram in a current of steam and conveying the distillate directly into 40 c.c. of N/2 potash. To test for galbanum resin, 5 grams is boiled with 15 grams of strong hydrochloric acid for 15 minutes, 15 c.c. of water is added, and the liquid filtered through a wetted, double filter; the clear filtrate is supersaturated with ammonia, when a blue fluorescence reveals the presence of galbanum. In estimating the saponification number, heat must be avoided. The following fractional method gives the resin number and gum number. Two quantities of 1 gram each are digested for 24 hours in stoppered flasks with 50 c.c. of light petroleum and 25 c.c. of normal alcoholic potash; one quantity is then diluted with 500 c.c. of water and titrated with N/2 sulphuric acid, which gives the resin number; whilst to the other, 25 c.c. of N/2 aqueous potash and 75 c.c. of water are added, and after another 24 hours the mixture is titrated as before, giving the saponification number. The difference is the gum number. A good specimen should show high acid and resin numbers, and a low gum number. M. J. S.

Detection and Estimation of Santonin in the Flower Buds of *Artemisia maritima*. By K. THAETER (*Arch. Pharm.*, 1897, 235, 401—414).—To estimate the quantity of santonin, the flowers are extracted with ether, the residue left on evaporating the ether is digested with milk of lime, the filtrate treated with aluminium acetate, excess of magnesia added, and the thoroughly dried mass again extracted with pure anhydrous ether. Three different kinds yielded 2.26, 2.43, and 2.78 per cent. of santonin respectively. The author finds that Kippenberger's method (*Ber. deutsch. pharm. Ges.*, 4), recommended by Thomas (*Zeit. anal. Chem.*, 34, 294), is not generally applicable owing to the extreme difficulty of extracting santonin by means of glycerol containing tannin.

Tannin precipitates santonin from aqueous but not from alcoholic solutions. With sulphuric acid alone, santonin does not give any coloration, but it is easily detected by means of furfuraldehyde sulphuric acid, with which it gives first a carmine-red coloration on warming, becoming bluish-violet, and finally dark blue; after prolonged digestion, a black precipitate is formed. By this means 0.0001 gram may easily be detected. The author has compared the effects of this test on a large number of alkaloids, bitter principles, glucosides, &c., but only the following gave characteristic colour reactions. α -Naphthol gives first a carmine-red and then a violet coloration which persists for an hour. β -Naphthol turns orange and then cherry-red. Veratrine gives various colours—green, red, blue—becoming violet, and finally brown; and with sulphuric acid alone a yellow, then carmine-red, and finally a brown colour. Picrotoxin with furfuraldehyde sulphuric acid produces a very persistent violet, and piperine a light-

green coloration, passing through sea-green to bluish-green and indigo blue. With sulphuric acid alone, the latter gives a reddish-yellow coloration which becomes brown on warming. E. W. W.

Caffeine, By GUILFORD L. SPENCER (*J. Amer. Chem. Soc.*, 1897, 19, 279—281).—The author prefers estimating caffeine in tea by means of Gomberg's volumetric iodine method (*Abstr.*, 1897, i, 129), instead of the gravimetric process. To obtain a suitable solution, 5 grams of finely ground tea is boiled for half an hour with about 400 c.c. of water; a considerable excess of recently prepared iron hydroxide is added, and after digesting for an hour the liquid is cooled and diluted to 500 c.c. An aliquot part is then filtered off and titrated by Gomberg's method.

L. DE K.

Modification of the Thalleioquinine Test for Quinine. By F. S. HYDE (*J. Amer. Chem. Soc.*, 1897, 19, 331—332).—Some of the suspected alkaloid (0.003—0.005 gram) is dissolved in 5 c.c. of water with the aid of one drop of dilute sulphuric acid (1:4), and a clear solution of bleaching powder is added until the blue fluorescence has just disappeared; a few drops of dilute ammonia (1:3) are then added, when a clear, emerald-green coloration should appear. This is more certain than the ordinary method of testing with chlorine or bromine water and ammonia.

L. DE K.

Behaviour of Proteids with Aldehydes. By ERNST O. BECKMANN with H. SCHARFENBERGER GEN. SERTZ and O. ELSNER (*Chem. Centr.*, 1896, ii, 930—932).—See this vol., i, 55.

Estimation of Albumin in Urine. By WASSILIEFF (*Chem. Centr.*, 1896, ii, 1012; from *St. Petersb. Wochenschr.*, 1896, 331).—For gravimetric estimation, the urine is mixed with 4 volumes of 95 per cent. alcohol, and the vessel immersed for 3—5 minutes in hot water. The precipitate is then collected, dried, weighed, and its ash (which never exceeds 1 per cent.) subtracted. For clinical purposes, albumin in urine can be titrated with salicylsulphonic acid. 10—20 c.c. of urine (acidified with acetic acid if alkaline) is diluted with water, mixed with 2 drops of a 1 per cent. aqueous solution of "Fast Yellow" (Echtgelb), and titrated with a 25 per cent. solution of salicylsulphonic acid until a permanent brick-red colour is obtained. One c.c. precipitates 0.01006 gram of albumin, and even at a dilution of 1:50000 produces a distinct turbidity.

M. J. S.

General and Physical Chemistry.

Validity of Maxwell's Equations. By P. S. WEDELL-WEDELLSBORG (*Zeit. physikal. Chem.*, 1897, 24, 367—370).—Known facts are, in the author's opinion, not in accord with Maxwell's equations, the validity of which is contested, for according to these equations, there must be, at the starting of a current, two induction effects: (1) that experimentally obtained; (2) that due to the increase of the electrostatic field. The paper also contains the author's reply to some of Goldhammer's criticisms of a previous paper on this subject (*Zeit. physikal. Chem.*, 23, 686).
L. M. J.

Laboratory Notes. By WILLIAM SKEY (*Chem. News*, 1897, 76, 109).—In the following couples, the electrolytes were separated by gelatin. With gold in potassium cyanide, and platinum in an acid, hydrogen is evolved from the platinum, but if an alkali is substituted for the acid, this is not the case. With gold or silver in cyanide, and gold or silver in copper sulphate, copper is deposited. With platinum or gold in tannic acid, and potash and platinum or gold in acid, a strong current is developed, and hydrogen is evolved until all the tannic acid is oxidised. Platinum in potash is positive to platinum in acid or ferrous sulphate, and throws down gold or platinum or silver from solution. Platinum in concentrated salt solution rendered alkaline with potash, and platinum in acid also throws down gold, from its chloride, on platinum and produces a strong current. An insulated voltaic cell connected with insulated silver plates 6 inches square and an inch apart in the air develops a current too feeble for detection by the galvanometer, but deposits gold, from its chloride, on platinum.
D. A. L.

Thermodynamics of "Swelling" ("Quellung"), with Special Reference to Starch and the Determination of its Molecular Weight. By HERMANN RODEWALD (*Zeit. physikal. Chem.*, 1897, 24, 193—218. Compare *Abstr.*, 1895, i, 165).—The author applies the term "swelling" to the absorption of water, or other liquid, by a solid substance which does not exhibit any pores, visible or microscopic. An expression is deduced thermodynamically for the heat liberated in terms of the change of specific volume, namely, $(1) \gamma = T[dp/dt(s' - s - y)]$, and the author then records the experimental work for the case of starch. Air-dried starch was found to contain about 16.33 per cent. of moisture, and the heat produced by soaking in water was observed for starches of different original water content, an ice-calorimeter being employed; a curve and table of the results are added. The contraction in volume was also obtained as a function of the percentage of water, the curve being very similar to the above heat curve. The values of dp/dt and y in the equation (1) are deduced from the values of the heat and volume change for the dry and moist starch, and the expression $\gamma = 273(s' - s)1.75 - 0.00507$ is thus obtained. A relation between the volume change, hence the heat of swelling, and the water content is next calculated, from which the equation $\log(s' - s) = 0.8 - 2 - 0.0423w$ is ob-

tained, and hence $\gamma = 0$ when $w = 31.63$. By means of an expression used by Kirchhoff for the vapour pressure of sulphuric acid solutions, that of the starch is calculated, the value thus obtained being 4.5594 for 31.63 per cent. of water; from this calculated value of the vapour pressure, the author deduces the number 4370 for the molecular weight of starch corresponding with the formula $C_{162}H_{270}O_{135}$. The expansion coefficient was found to be a linear function of the water, and the force of attraction between dry starch and moisture is calculated as 2073 kilos. per sq. cm.

L. M. J.

Distillation with Vapour. By C. H. BENEDICT (*J. Physical Chem.*, 1897, 1, 397—402).—The author finds that there is an enormous increase in the volatility of solid naphthalene when ether is present. Distillation with a current of ether vapour would give not less than four times as much naphthalene as if the process were carried on with an air current or under diminished external pressure. Some rough measurements with camphor in different solvents gave similar results.

H. C.

Solubility of Solids in Vapours. By J. M. TALMADGE (*J. Physical Chem.*, 1897, 1, 547—554).—The author distilled saturated solutions of camphor and naphthalene in methylic alcohol, ethylic alcohol, acetone, and ether under different pressures, an excess of the solid being present in all cases. In the case of naphthalene, he was unable to confirm Benedict's result (see preceding abstract), and although the experiments show that the concentration of naphthalene vapour in equilibrium with solid naphthalene is not independent of the other components in the system, they do not show whether the vapour pressure is increased or decreased by the presence of a solvent. In the case of camphor, the vapour pressure of the solute also varies with the solvent. The values with ether and acetone are more than double the real vapour pressures. With methylic alcohol, the values are a little above the normal, whilst with ethylic alcohol, the calculated vapour pressures are only about one-half of those obtained directly.

H. C.

Temperature of Maximum Density of Barium Chloride Solutions. By LOUIS C. DE COPPET (*Compt. rend.*, 1897, 125, 533).—The following results were obtained.

BaCl ₂ in 1000 grams of water.	Temperature of maximum density.	Reduction of the temperature of maximum density.	Molecular reduction of temperature of maximum density.
0	3.982°	—	—
6.73	3.207	0.775°	23.94
10.42	2.785	1.197	23.88
20.83	1.572	2.409	24.04
41.72	-0.843	4.825	24.04

The reduction of the temperature of maximum density is sensibly proportional to the weight of anhydrous barium chloride dissolved in 1000 grams of water.

C. H. B.

Solubilities of Liquids. By A. AIGNAN and E. DUGAS (*Compt. rend.*, 1897, 125, 498—500).—Mixtures of acetic acid and benzene in various proportions become homogeneous at different temperatures.

Acetic acid	30 c.c.	40 c.c.	50 c.c.	60 c.c.	70 c.c.
Benzene.....	70 c.c.	60 c.c.	50 c.c.	40 c.c.	30 c.c.
Temperature of } homogeneity }	102°	75°	50°	30°	2.5°

and in these cases it is difficult to decide which is the solvent and which the dissolved substance, as in the case of aniline, phenol and water described by Alexéeff (Abstr., 1886, 847), and his method of observation does not admit of the solution of the problem.

If V_a and V_b are the respective volumes of the two liquids A and B introduced into the sealed glass tube, α and β their coefficients of reciprocal solubility, and V_1 and V_2 the respective volumes of the two layers of liquid, A saturated with B and B saturated with A,

$$\frac{V_1}{V_2} = \frac{1 + \beta}{1 + \alpha} \cdot \frac{V_a - \alpha V_b}{V_b - \beta V_a},$$

and a similar relation holds good if weights are taken instead of volumes. When the temperature varies, if α tends towards the value V_a/V_b , the numerator of the first member V_1 should tend towards zero; but if β tends towards the value V_a/V_b , then V_2 should tend towards zero. It becomes necessary, therefore, to observe towards which extremity of the tube the surface of separation of the liquids disappears on heating.

In the cases quoted, with 30, 40, or 50 per cent. of acetic acid, the surface of separation tends towards the bottom of the tube, and hence at 75° and 50° saturated solutions of acetic acid in benzene occur; with 60 and 70 per cent. of acetic acid, the surface of separation tends to disappear towards the upper part of the tube, and hence at 30° and 2.5° saturated solutions of benzene in acetic acid occur.

The authors criticise Alexéeff's method of drawing his curves, which they regard as based on an erroneous assumption.

C. H. B.

Kinetic Theory of Solutions. By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1897, 24, 366).—In his paper on osmotic pressure (Abstr., 1897, ii, 395), the author erroneously ascribed an inaccurate expression to Nernst.

L. M. J.

Osmotic Pressure and Variance. By JOSEPH E. TREVOR (*J. Physical Chem.*, 1897, 1, 349—365).—The variance is always the total number of variables which a system exhibits, diminished by the number r of its phases. The variables are n potentials, being at least one for each independently variable component, one for the temperature, and one for at least one pressure, with x for the added pressures introduced by the appearance of x osmotic walls, and y for each of the y separations of a component by such a wall. The total number of variables is, therefore, $n + 2 + x + y$, and the variance is $v = n + 2 + x + y - r$. This is the generalised phase rule as applicable to all systems containing osmotic pressures. For the limiting case in which all osmotic walls are absent, we have both $x = 0$ and $y = 0$, and consequently the Gibbs' variance of $v = n + 2 - r$.

H. C.

Variance of Osmotic Systems. By JOSEPH E. TREVOR (*J. physical Chem.*, 1897, 1, 537—541).—The author shows how it is possible to realise for two component monovariant systems the anticipated set of five curves of osmotic pressures, and their intersection at a five-fold multiple point (compare preceding abstract). H. C.

The Phase Rule and the Physical Properties of Chemical Compounds. By F. WALD (*Zeit. physikal. Chem.*, 1897, 24, 315—324).—The author discusses the well-known phase-law of Gibbs, namely, $v = n + 2 - r$, where r is the number of phases, v the number of independent variations, and n that of the independent components, two physical conditions only changing. The case chiefly considered is that for an equal number of phases and components, and the author regards it as proved that a number of physical relations "may be deduced between the substances entering into a reaction, especially Gay Lussac's gas law of rational volume ratios." L. M. J.

Quintuple Points. By WILDER D. BANCROFT (*J. Physical Chem.*, 1897, 1, 337—343).—In a system composed of two salts and water there will be in equilibrium at the quintuple points three solid phases, solution, and vapour. The various quintuple points can be classified under three heads.

I. Two of the solid phases can be made from the third with addition or subtraction of water.

II. One of the solid phases can be transformed into one of the others by addition or subtraction of water.

III. No one of the solid phases can be converted into either of the others by addition or subtraction of water.

When one of the solid phases can change into the other two with addition or subtraction of water, the inversion point is a minimum temperature for that phase if the water be added to complete the reaction, and a maximum if the water be subtracted. If one of the solid phases can be converted into one of the others by addition of water, the inversion point is a maximum or a minimum temperature for one of those phases, and is neither a maximum nor a minimum for the third solid phase. When no one of the solid phases can be converted into either of the others by addition or subtraction of water, no prediction can be made. There cannot be in equilibrium three solid phases such that one can be made from the other two without addition or subtraction of water. H. C.

Solids and Vapours. By WILDER D. BANCROFT (*J. Physical Chem.*, 1897, 1, 344—348).—Whilst many salts in efflorescing at constant temperature form all intermediate hydrates, this is not always the case. For example, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ changes normally to the anhydrous salt without formation of $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$. If we start with hydrated sodium sulphate, solution, and vapour, and raise the temperature to about 33° , the anhydrous salt will be formed. On decreasing the external pressure, the solution will disappear, leaving the stable monovariant system, hydrated and anhydrous sodium sulphate and vapour. Decreasing the pressure yet more, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ must effloresce with formation of the anhydrous salt. Were it to form

the heptahydrated salt, there would be present a non-variant system. This would also be formed from the monovariant system at any other temperature at which the latter could exist, and we should thus have the phenomenon of a non-variant system existing at a series of temperatures and pressures, which is impossible according to the phase rule. From this it follows that a solid phase containing two components effloresces with formation of the solid phase which can co-exist at the next higher quadruple point. Two solid phases containing three components effloresce with formation of the solid phase which can co-exist at the next higher quintuple point. From a study of the efflorescence products, one can draw conclusions as to the phases existing at the quintuple points.

H. C.

A Triangular Diagram [to represent Composition-Temperature Changes]. By WILDER D. BANCROFT (*J. Physical Chem.*, 1897, 1, 403—410).—A diagram consisting of an equilateral triangle with lines ruled parallel to each side, instead of perpendicular to them, was proposed by Roozeboom for the representation of the changes in composition of a given phase with the temperature when there are three components. The author points out some geometrical relations connected with the use of this diagram.

H. C.

Two Liquid Phases. By WILDER D. BANCROFT (*J. Physical Chem.*, 1897, 1, 414—425).—The author considers the general case of quintuple points with two solid phases, two liquid phases and vapour, formed by adding a component *C* to two components *A* and *B* such that there can be formed the quadruple point, solid *A*, two solutions, and vapour. The general results are.

1. The component *C* dissolves in *B* with precipitation of *A*. The freezing point rises. The solid phases at the quintuple point are *A* and *C* or else no non-variant system with two liquid phases is possible.

2. The component *C* dissolves in *A* with precipitation of *B*. The freezing point falls. There is one quintuple point with *A* and *C* as solid phases, or two with *A* and *B*, *B* and *C* as solid phases, or one with *A* and *B* as solid phases.

3. The component *C* increases the miscibility of *A* and *B*; the freezing point falls. There is one quintuple point with *A* and *C* as solid phases, or one with *A* and *B* as solid phases, or there is formed the divariant system, solid *A*, solution, and vapour.

4. If the component *C* dissolves in *A* with precipitation of *B* and there are two quintuple points, the one with *B* and *C* as solid phases will exist at a higher temperature than the one with *A* and *B* as solid phases.

5. If the component *C* increases the miscibility of *A* and *B* and there are two quintuple points, the one with *B* and *C* as solid phases exists at a lower temperature than the one with *A* and *B* as solid phases.

H. C.

Solubility and Freezing Point. By DOUGLAS MCINTOSH (*J. Physical Chem.*, 1897, 1, 474—492).—When we have two non-miscible substances *A* and *C* and a third substance *B* with which the other two are miscible we can distinguish two cases.

In the first case, the component *A* can exist as solid phase under the conditions of the experiment. Under these circumstances, addition of *C* to the liquid phase containing *A* and *B* will raise the temperature at which *A* can exist as solid phase. In other words, addition of a substance to a binary solution in equilibrium with a solid phase raises the freezing point if the substance added be non-miscible with the component appearing as solid phase. This is shown to be the case for an alcohol-benzene solution to which water is added.

In the second case, the component *B* can exist as solid phase under the conditions of the experiment. Under these circumstances, addition of *B* to the liquid phase containing *A* and *B* will lower the temperature at which *B* can exist as solid phase, and this lowering will be more than it would be if *A* and *C* were miscible to some extent. When the three components are miscible, the sum of the single depressions is usually greater than the depression for the mixture; but this is not always true, owing to disturbing conditions which are not yet defined.

H. C.

Mass Law Studies, II., III. By S. F. TAYLOR (*J. Physical Chem.*, 1897, 1, 461—473 and 542—546).—In order to study a case in which two liquid phases and a vapour phase are present, the author has analysed six mixtures of benzene, water, and alcohol. The general form of the relations for this system is deduced from the mass law, and it is shown that one must use mass concentrations and not volume concentrations in expressing the distribution of a substance between two liquid phases. Agreement of theory and experiment is obtained in the case studied, and the theory is also successfully applied to the system chloroform, water, and acetic acid.

H. C.

Hydrolytic Dissociation. By HEINRICH LEY (*Ber.*, 1897, 30, 2192—2196).—The author makes a preliminary communication of results obtained in an investigation of the hydrolysis of salts in aqueous solution. The concentration of the hydrogen ions is determined by measuring the velocity of inversion of cane-sugar by the salt solution at 100°. The following numbers were obtained with solutions of aluminium chloride containing 1 gram equivalent in *v* litres, *p* being the percentage hydrolysed.

<i>v.</i>	<i>p.</i>		<i>v.</i>	<i>p.</i>
32	8.8		256	28.7
64	13.8		512	41.8
128	20.1			

Aluminium sulphate is hydrolysed to a smaller extent.

Zinc chloride and sulphate exhibit a similar relationship, the latter salt undergoes very little dissociation, the hydrolysis reaching 0.03 per cent. in 1/16 normal solution.

Lead and copper chlorides gave abnormal results, the rate of inversion of the sugar increasing with the duration of the experiment.

Mercuric chloride could not be examined by this method, because it is reduced by sugar. By assuming that its electrical conductivity is entirely due to the hydrochloric acid produced by its hydrolysis, an

upper limit for the latter is obtained varying from 0.29 per cent. in 1/16 normal to 1.64 per cent. in 1/256 normal solution.

The addition of potassium chloride to a solution of aluminium chloride diminishes the hydrolytic dissociation of the latter. The same is true of other salts; the acid reaction of solutions of lead or mercuric chloride disappears when sodium or potassium chloride is added to them. T. E.

Formation of Anilides. By HEINRICH GOLDSCHMIDT and CURT WACHS (*Zeit. physikal. Chem.*, 1897, 24, 353—365).—It has been shown by Goldschmidt and Reinders that, in solutions of aniline salts in aniline, the salt is probably decomposed into acid and base (Abstr., 1896, ii, 556), a part of the acid being further dissociated. The formation of an anilide is hence analogous to that of an ethereal salt, that is, should be a bimolecular reaction unless a strong acid be added, in which case it becomes monomolecular with velocity proportional to the concentration of the catalysing acid (Abstr., 1896, ii, 638). Experiments with aniline and acetic or propionic acid, and with orthotoluidine and acetic acid showed the reaction to be bimolecular; on the addition of picric, hydrochloric, or hydrobromic acid, it becomes monomolecular, the velocity being accelerated, and proportional to the concentration of the strong acid if sufficiently great. The reaction being bimolecular is not a proof of the non-occurrence of autocatalysis as stated by Donnan (Abstr., 1897, ii, 15) since, if x is the quantity of acid converted into anilide, then $(a-x)$ is the concentration of the acid, and is also proportional to the concentration of the hydrogen ions, so that the velocity is proportional to $(a-x)^2$. The analogy of these solutions to those of hydrated salts is again noticed, and the view that, in solution, the latter are present as anhydrides thus receives support. L. M. J.

Genesis of Dalton's Atomic Theory. By HEINRICH DEBUS (*Zeit. physikal. Chem.*, 1897, 24, 325—352).—The author upholds his previously published views (Abstr., 1896, ii, 639) regarding the origin of Dalton's theory, that is, that Avogadro's law was held and employed by Dalton, who definitely states that in 1801 he had a "confused idea" that all molecules were of equal size; hence that $M/d=k$. He, moreover, made frequent use of this hypothesis; thus the ratio of the atomic weights of oxygen and nitrogen was fixed at 6/7 from the consideration of their densities, whilst, further, of the gases nitric oxide, nitrous oxide, and "nitric acid," the first has the lowest density and therefore consists "of but two atoms," and since "nitric acid" is heavier than nitrous oxide, it follows that "an atom of oxygen is heavier than an atom of nitrogen." The author points out that this reasoning is entirely dependent on the assumption that the "atomic" (that is, molecular) weight is proportional to the density; in other words, that $M/d=k$. Other similar cases occur, but the apparent failure of this mode of calculation in the case of the hydrocarbons, due to erroneous ideas regarding their composition, ultimately led Dalton to abandon this hypothesis as not of general, although of frequent, application. The second part of the paper is entirely a review,

criticism, and refutation of various passages in the reply of Roscoe and Harden to the previous paper (*Zeit. physikal. Chem.*, **22**, 241).

L. M. J.

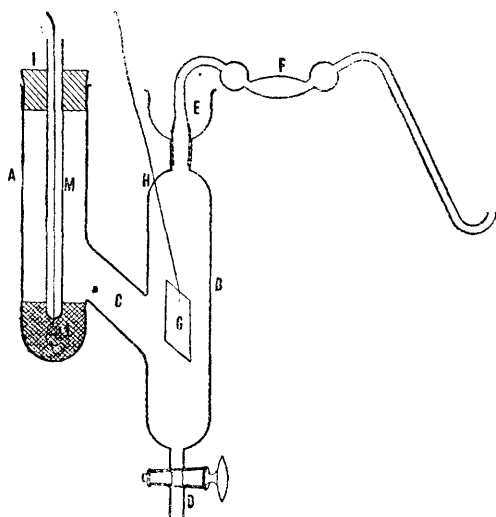
Lecture Apparatus. By WILLIAM R. E. HODGKINSON (*Chem. News*, 1897, **76**, 152).—Volumemeter. A cylindrical vessel of 100 c.c. capacity provided with a deep and broad, hollow, tubulated stopper is connected at its lower end, by a narrow tube having a stopcock, with a graduated tube. It is filled with the liquid to be used from the zero of the graduated tube to a mark made on the tube of the stopper. After the liquid has been driven into the graduated tube, the stopper is carefully removed, the substance whose volume is to be measured introduced, the stopper replaced, and the liquid brought back to the mark on the stopper. The volume of the substance can now be read off on the graduated tube.

For showing that hot water boils in a closed flask when cold water is poured over it, an improved form of apparatus is described consisting of a fractionating flask with a stopcock sealed on the side tube, and a wide thermometer, wedged by a rubber ring in the neck, with its bulb just dipping into the hot water.

D. A. L.

Inorganic Chemistry.

New Form of the Hydrogen Generator. By E. W. MAGRUDER (*Amer. Chem., J.*, 1897, 19, 810—812).—The apparatus consists of a



tube B, furnished at the bottom with the stopcock D, and at the top with the funnel E, into which fits, with a ground joint, the delivery-tube F. B also contains a platinum electrode G, suspended by a platinum wire fused through the tube at H. Zinc amalgam is put into A until it nearly reaches the tube C, A being then closed with a rubber stopper I, carrying a glass tube M, containing a platinum wire, fused through the tube at L and dipping into the amalgam. The apparatus

may be simplified by leaving out the stopcock D, and fusing F directly to the top of B.

As the oxygen and hydrogen electrodes are in separate tubes, oxygen or any other escaping gas simply rises to the surface in A, and does not, therefore, mix with the hydrogen.

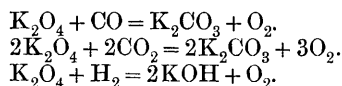
By having the amalgam nearly up to the side tube, the zinc sulphate formed flows into B, from which it can be drawn off through the stop-cock. The generated gas is perfectly pure hydrogen. A. W. C.

Nascent Hydrogen. By DONATO TOMMASI (*J. Physical. Chem.*, 1897, 1, 555).—A priority claim in connection with Franchot's work on nascent hydrogen (*Abstr.*, 1897, ii, 138).

WILDER D. BANCROFT (*ibid.*, 1897, 1, 556) replies by pointing out that Franchot's work had not reached the point at which one would naturally make a reference to Tommasi. H. C.

Heat of Dissociation of Iodine. By JOACHIM SPERBER (*Zeit. anorg. Chem.*, 1897, 15, 281—282).—The heat of dissociation of iodine, calculated according to the author's theory (*Abstr.*, 1897, ii, 307), is 13·132 Cal.; he points out that this is in close agreement with the number obtained by Boltzmann, namely, 14·265 Cal. E. C. R.

Evolution of Oxygen during Reduction. By K. FRENZEL, S. FRITZ and VICTOR MEYER (*Ber.*, 1897, 30, 2515—2519. Compare *Abstr.*, 1897, ii, 19, 93; this vol. ii, 19).—Erdmann (*Abstr.*, 1897, ii, 97) has attempted to explain the evolution of oxygen during the reduction of rubidium dioxide by hydrogen by the intermediate formation of hydrogen peroxide; in order to test this, experiments were made in some of which such formation was impossible. Potassium peroxide yields no oxygen when heated to the softening point of glass (in a silver vessel) in a current of air. In carbonic oxide, carbonic anhydride, and hydrogen, on the other hand, it gives a considerable amount of oxygen at the boiling point of sulphur. In the cases of carbonic oxide and anhydride, the intermediate formation of hydrogen peroxide is excluded, and it is probable that the three reactions are quite analogous.



Silver oxide decomposes in a current of air at 250°, but when heated at the boiling point of water in hydrogen, it yields free oxygen, and does this even at the ordinary temperature in carbonic oxide; this is due to the fact that the heat evolved by the reduction of a portion of the oxide is so great as to raise the temperature of the rest above the point of decomposition. Similar results were obtained with potassium permanganate, which decomposes in air at 218°, and in hydrogen to a very small extent at 155°, freely at 182°. No evolution of oxygen was observed during the reduction of barium peroxide. A. H.

Solubility of Ammonia in Water at Temperatures below 0°. By JOHN W. MALLETT (*Amer. Chem. J.*, 1897, 19, 804—809).—On pass-

ing gaseous ammonia into an already strong aqueous solution at temperatures below 0° , the following results were obtained.

At -10°	1 gram of water dissolves	1.115 grams of ammonia		
" -20	"	"	1.768	"
" -30	"	"	2.781	"
" -40	"	"	2.946	"

No visible change marks the presence of enough ammonia to represent the hydroxide of ammonium, assumed to exist in ordinary solution, and the hydroxide, if it exists, continues to dissolve ammonia, or mixes with liquefied ammonia down to and beyond the normal boiling point of the latter.

The proportion of ammonia dissolved by water is much greater than would be called for by an extension of the curve representing the solubility at temperatures above 0° . A. W. C.

Chloronitrides of Phosphorus. II. By HENRY N. STOKES (*Amer. Chem. J.*, 1897, 19, 782—796. Compare Abstr., 1895, ii, 217).—Continuing his researches on the chloronitrides of phosphorus, the author finds they are best prepared by heating phosphorus pentachloride and ammonium chloride, in molecular proportion, in sealed tubes, $\text{PCl}_5 + \text{NH}_4\text{Cl} = \text{PNCl}_2 + 4\text{HCl}$. The operation requires to be conducted with great caution on account of the large amount of hydrogen chloride generated. There is formed a mixture of chloronitrides, which is partly crystalline and soluble in light petroleum, and partly liquid and insoluble in this solvent; the latter portion consists of about 50 per cent. $\text{P}_3\text{N}_3\text{Cl}_6$ and 25 per cent. $\frac{1}{2}\text{P}_4\text{N}_4\text{Cl}_8$, the remainder consisting of the higher homologues. A separation is effected by means of fractional distillation, and, in the case of the solids, crystallisation from benzene.

The series, as at present known, consists of the following.

	Melting point.	Boiling point.	
		13 mm.	760 mm.
<i>Triphosphonitric chloride</i> , $(\text{PNCl}_2)_3$	114°	127°	256.5°
<i>Tetraphosphonitric chloride</i> , $(\text{PNCl}_2)_4$	123.5°	188°	328.5°
<i>Pentaphosphonitric chloride</i> , $(\text{PNCl}_2)_5$	$40.5-41^{\circ}$	$223-224.3^{\circ}$	polymerises
<i>Hexaphosphonitric chloride</i> , $(\text{PNCl}_2)_6$	91°	$261-263^{\circ}$	polymerises
<i>Heptaphosphonitric chloride</i> , $(\text{PNCl}_2)_7$	liquid at -18°	$289-294^{\circ}$	polymerises
<i>Polyphosphonitric chloride</i> , $(\text{PNCl}_2)_x$	below red heat	depolymerises on distillation	

There were obtained, further, a liquid residue of the same empirical composition with a mean molecular weight of $(\text{PNCl}_2)_{11}$ and a small amount of *nitrihexaphosphonitric chloride*, $\text{P}_6\text{N}_7\text{Cl}_9$, not belonging to the above series. It melts at 237.5° (corr.) and boils at $251-261^{\circ}$ (13 mm.), crystallises in transparent rhombic prisms, often united to acicular forms, and when pulverised becomes electrified.

The complete absence of the lower members of the above series

PNC_2Cl_2 and $(\text{PNC}_2\text{Cl}_2)_2$ is very remarkable. Each member of the series is converted by heat into the caoutchouc-like polyphosphonitrilic chloride, which is highly elastic and insoluble in all neutral solvents. It swells enormously in benzene, and on heating breaks down into a mixture of all the lower members mentioned above.

A. W. C.

Migrant Matter. By STEPHEN H. EMMENS and NEWTON W. EMMENS (*Chem. News*, 1897, **76**, 37).—Minute variations in weight observed in little discs, one of silver and one of lead (free from silver), suspended in air in a bottle and both in contact with the same spiral of copper wire are attributed to migration of matter. On cupellation, the lead now showed a minute amount of silver.

D. A. L.

Valency of Beryllium. By ARTHUR ROSENHEIM and PAUL WOGEL, (*Zeit. anorg. Chem.*, 1897, **15**, 283—318). Hydrated beryllium oxide, when treated with solutions of oxalic acid and hydrogen alkali oxalates, yields a series of double salts and not complex compounds as in the case of the hydrated oxides of chromium, iron, and aluminium. When treated with hydrogen alkali tartrates, it yields a series of complex compounds of the formula $\text{R}_2\text{O}, 4\text{BeO}, 2\text{C}_4\text{H}_4\text{O}_5 + 8\text{H}_2\text{O}$, in which beryllium displaces the hydroxyl hydrogen atom of the tartaric acid. When treated with salts of paramolybdic acid, it yields beryllium molybdate, $\text{BeO}, \text{MoO}_3 + 2\text{H}_2\text{O}$, and with hydrogen alkali sulphites it yields characteristic crystalline double salts. All these reactions point to the conclusion that beryllium is bivalent; and the determination of the molecular weight of beryllium chloride by Beckmann's boiling point method, using pyridine as the solvent, gives numbers which agree closely with the formula BeCl_2 .

The double salts, $\text{K}_2\text{O}, 2\text{BeO}, 2\text{C}_2\text{O}_3 + 2\frac{1}{2}\text{H}_2\text{O}$; $\text{Na}_2\text{O}, 2\text{BeO}, 2\text{C}_2\text{O}_3 + 5\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{O}, 2\text{BeO}, 2\text{C}_2\text{O}_3 + 2\frac{1}{2}\text{H}_2\text{O}$, are obtained by treating a boiling solution of potassium, sodium, and ammonium oxalate respectively with hydrated beryllium oxide. The potassium salt separates in lustrous crystals, the sodium salt, which is very soluble, in ill-defined crystals, and the ammonium salt in slender needles; the two former are stable on exposure to the air, but the ammonium salt is extremely hygroscopic. Oxalic acid and beryllium can be detected in solutions of these salts by the ordinary methods.

The salts $\text{K}_2\text{O}, \text{BeO}, 2\text{C}_2\text{O}_3 + \text{H}_2\text{O}$; $\text{Na}_2\text{O}, \text{BeO}, 2\text{C}_2\text{O}_3 + \text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{O}, \text{BeO}, 2\text{C}_2\text{O}_3$ are obtained by saturating solutions of the corresponding hydrogen alkali oxalates with hydrated beryllium oxide, and then adding an equal quantity of the hydrogen alkali oxalate. When treated with calcium or barium chloride, they are quantitatively decomposed into calcium or barium oxalate and beryllium chloride. When boiling oxalic acid is saturated with hydrated beryllium oxide, a non-crystallisable syrup is obtained containing 1 mol. of oxalic anhydride to 2.5—3 mols. beryllium oxide; if to this solution an equal quantity of oxalic acid is added, *beryllium oxalate*, $\text{BeOC}_2\text{O}_3 + 3\text{H}_2\text{O}$, separates in needles, which are obtained in quadratic tablets on recrystallisation from water. The *acid oxalate*, $2\text{BeO}, 3\text{C}_2\text{O}_3 + 6\text{H}_2\text{O}$, is obtained by dissolving 1 mol. of beryllium oxide in 2 mols. of oxalic acid. It crystallises in beautiful prisms.

The *complex tartrates*, $\text{K}_2\text{O}, 4\text{BeO}, 2\text{C}_4\text{H}_4\text{O}_5 + 8\text{H}_2\text{O}$, the sodium salt

with $8\text{H}_2\text{O}$, and the ammonium salt with $8\text{H}_2\text{O}$, are obtained by saturating a boiling aqueous solution of the corresponding hydrogen, alkali tartrate with hydrated beryllium oxide. The potassium salt, which is extremely soluble, crystallises in large, lustrous prisms, the sodium and ammonium salts in microcrystalline crusts; the beryllium in these salts is at once precipitated by ammonia. However, the complex character of the salts is shown in the abnormal behaviour of the tartaric acid. Potassium chloride does not cause a precipitation of potassium tartrate, even on adding dilute acids; no precipitate is obtained with calcium chloride, and barium chloride gives a precipitate only after some time. With neutral silver nitrate, a flocculent, voluminous precipitate is at once formed. All the salts are neutral to ordinary indicators.

These salts are the first compounds isolated in which a metal is substituted for, not only the carboxyl hydrogen atom, but also for the hydroxyl hydrogen atom of the tartaric acid.

The salt $\text{K}_2\text{O}, 2\text{BeO}, 2\text{C}_4\text{H}_4\text{O}_5 + 2\text{H}_2\text{O}$, obtained by dissolving the theoretical quantity of hydrated beryllium oxide in a solution of hydrogen potassium tartrate, forms a glassy, crystalline mass, and has properties similar to those of the preceding beryllium tartrates; it is strictly analogous to the copper compound of Fehling's solution.

Beryllium molybdate, $\text{BeOMoO}_3 + 2\text{H}_2\text{O}$, obtained by boiling the theoretical quantity of hydrated beryllium oxide with molybdic acid suspended in water, is an oily liquid which solidifies to an aggregate of slender needles if kept for some time in the cold.

The complex compounds corresponding with those obtained by saturating potassium or sodium paramolybdate with sesquioxides cannot be obtained in the case of beryllium oxide, beryllium paramolybdate being always formed. With ammonium paramolybdate, beryllium molybdate is usually formed, but in some cases the double salt, $10(2\text{BeO}, \text{MoO}_3) + 2(\text{NH}_4)_2\text{O}, 3\text{MoO}_3 + 18\text{H}_2\text{O}$ is obtained, crystallising in microcrystalline crusts.

The double salts, $\text{K}_2\text{O}, 2\text{BeO}, 3\text{SO}_2 + 9\text{H}_2\text{O}$ and
 $(\text{NH}_4)_2\text{O}, 2\text{BeO}, 3\text{SO}_2 + 4\text{H}_2\text{O}$,

are prepared by digesting freshly prepared solutions of the hydrogen alkali sulphites with hydrated beryllium oxide on the water bath; the solutions, which must contain excess of sulphurous acid, yield crystals of the salts on cooling. They are extremely easily oxidised, and when exposed to the air rapidly evolve sulphurous anhydride, ammonium sulphite being also formed.

E. C. R.

Potassium Lead Iodide. By J. M. TALMADGE (*J. Physical Chem.*, 1897, 1, 493—498).—Schreinemakers (Abstr., 1893, ii, 260) has shown that concentration at ordinary temperatures of a solution from which the solid double salt $\text{PbI}_2, \text{KI} + 2\text{H}_2\text{O}$ has separated is always attended by solution of the double salt. The author shows that, at 100° , the behaviour is reversed and there is continued precipitation of the double salt on evaporation.

H. C.

Cuprous Chloride. By J. K. HAYWOOD (*J. Physical Chem.*, 1897, 1, 411—413).—Lescœur has shown that when cuprous chloride is

treated with water, cuprous oxide and hydrochloric acid are formed, and states that when cuprous chloride is washed with water, the amount of acid in the wash water remains practically constant until all the cuprous chloride has been converted into oxide. The author shows that this last result must have been obtained by accident, as the action is dependent on time and the mass of water present. H. C.

Possible New Element or Elements in Cast Iron and Blast-furnace Boiler-Dust. By GETHEN G. BOUCHER (*Chem. News.*, 1897, 76, 99—100; 182).—The suspected new metal has been obtained from iron to the extent of from 0.0019 to 0.006 per cent., in the following manner. The iron is treated with dilute 1:5 sulphuric acid and the cold solution saturated with hydrogen sulphide. The mixed precipitate and undissolved matter, after being washed until free from iron, is boiled with hydrochloric acid and potassium chlorate until the evolution of chlorine ceases, and the filtered solution is saturated with hydrogen sulphide. The precipitate is again submitted to the treatment with hydrochloric acid and potassium chlorate; the arsenic precipitated by magnesia mixture and filtered off; the copper, by treatment with hydrogen sulphide, precipitated as sulphide, which is removed, and the solution slightly acidified with hydrochloric acid. The precipitate is repeatedly boiled with hydrochloric acid to remove antimony sulphide and a heavy dark-brown sulphide remains. This is dissolved in potash, the solution treated with hydrogen sulphide, filtered, and reprecipitated with hydrochloric acid, these operations being repeated until no further precipitate is obtained from the alkaline solution on treatment with hydrogen sulphide. The sulphide is dissolved in hot (1:2) nitric acid, the solutions filtered, made slightly alkaline with ammonia, any precipitate removed, and the metal again precipitated as sulphide.

The *metal* is obtained as a black powder by reducing the oxide in a current of hydrogen, or by fusion with potassium cyanide; it is insoluble in dilute hydrochloric and sulphuric acids, sparingly soluble in these acids when strong, is soluble in dilute and strong nitric acid, and very readily soluble in aqua regia. When heated in a current of air, the metal glows and forms a yellow, volatile oxide. The *oxide*, which is also formed on roasting the sulphide, melts at a low temperature and sublimes at a full red heat, yielding transparent, colourless needles; it is sparingly soluble in hydrochloric acid, almost insoluble in sulphuric acid, and insoluble in nitric acid. The borax bead is clear and colourless in the outer, and pale pink in the inner, flame, the microcosmic salt beads are chrome-green, that in the inner flame being darker. When fused with sodium carbonate, the oxide yields a colourless mass soluble in water. The *sulphide*, precipitated from slightly acid solutions by hydrogen sulphide, is dark-brown, and soluble in the sulphides of ammonia and sodium and in the alkali hydroxides, also in nitric acid and aqua regia, but insoluble in dilute hydrochloric and sulphuric acids. The solution of the chloride gives the following reactions: with sodium thiosulphate, a violet coloration, turning brown on heating with hydrochloric acid and yielding a precipitate of the sulphide; with potassium ferricyanide, a dark brown, flocculent precipitate soluble in acids and alkalis; with alkali hydroxides, a slight blue coloration, with zinc or iron, a black deposit of metal, some of which escapes with

the evolved hydrogen; and when deposited in the usual way from the flame, is almost black with little lustre, and neither soluble in hydrochloric acid nor calcium hypochlorite. No reactions, however, are obtained with carbonates, chlorides, sodium sulphate, phosphate or acetate, magnesia mixture, potassium cyanide, ferrocyanide or chromate, ferrous sulphate or stannous chloride. The chloride or nitrate when evaporated nearly to dryness with hydrochloric or, better still, sulphuric acid, gives a blue coloration destroyed by water. It does not give a precipitate when warmed with sodium phosphate and nitric acid.

Heavy, dark-coloured boiler-dust yields a metal that is similar in all respects except that, with stannous chloride, it produces a dark blue colour, turning brown when boiled with hydrochloric acid. The strong aqueous extract of the dust is treated with hydrogen sulphide and hydrochloric acid, the precipitate, when sufficient has been accumulated, is dissolved in aqua regia and evaporated nearly to dryness with sulphuric acid; the solution is diluted, filtered, made alkaline with ammonia, treated with hydrogen sulphide, filtered, and acidified with hydrochloric acid. The precipitated sulphide is dissolved in potash and treated as in the preceding case. A ton of dust yielded 0.3 gram of this metal.

D. A. L.

Lucium. By WALDRON SHAPLEIGH (*Chem. News*, 1897, '76, 41).—Following Barrière's methods, but making each separation thoroughly, the author did not obtain lucium from monazite, but, instead, less than 1 per cent. of mixed oxides of the yttria group. He remarks that concentrated solutions of yttrium potassium sulphate give a precipitate when heated, and suggests that this may be the origin of Barrière's lucium, inasmuch as Barrière used concentrated solutions, and then heated (compare Crookes, *Abstr.*, 1897, ii, 144).

D. A. L.

Action of Carbonic Anhydride on Sodium Aluminate. Formation of Basic Aluminium Carbonate. By WILLIAM C. DAY (*Amer. Chem. J.*, 1897, 19, 707—728).—When carbonic anhydride is passed into a solution of sodium aluminate (prepared from "Connetable" phosphate rock by the action of quicklime and sodium carbonate, and subsequent washing), a precipitate is formed which differs from aluminium hydroxide precipitated from an aluminium salt by means of ammonium hydroxide in being of an opaque white, and more granular. If this precipitate is washed with cold water until the washings show no alkaline reaction, and the air-dried residue is analysed, it is found to contain more carbonic anhydride (from 5.5—9 per cent.) than is capable of uniting with the small amount of sodium present.

The author concludes that this substance must be regarded as a basic aluminium carbonate. The literature bearing on this subject is discussed at some length.

A. W. C.

[Reactions of Titanic Acid with Organic Acids.] By GEORG BERG (*Zeit. anorg. Chem.*, 1897, 15, 328—330).—See this vol., i, 66.

Platino-platinoso-additive Compounds. By MAURICE VÈZES (*Zeit. anorg. Chem.*, 1897, 15, 278—280).—The author points out that acid potassium triplatinosohexanitrite, $\text{Pt}_3\text{O}(\text{NO}_2)_6\text{K}_2\text{H}_4$, which he obtained by the cautious oxidation of potassium platinosonitrite, cannot have a constitution analogous to the platinum compounds described

by Werner (Abstr., 1896, i, 465) and Hadow (this Journal, 1860, 13, 106), although it exhibits the same phenomenon, namely, it crystallises in copper-coloured crystals and gives an almost colourless solution in water. The same behaviour is characteristic of the compound obtained by Miolati by heating at 150° the compounds $\text{Pt}(\text{NO}_2)_4\text{K}_2\text{N}_2\text{O}_4$ and $\text{Pt}(\text{NO}_2)_4\text{K}_2\text{HCl}$. Miolati states that it is identical with, or analogous to, acid potassium triplatinohexanitrite. E. C. R.

Mineralogical Chemistry.

Critical Review of Methods of Determining Minerals. By JOSEPH W. RICHARDS (*Chem. News*, 1897, 76, 114—116, 139—140).—The author comments on Dana's, Weissbach's, Von Kobell's and Fuch's schemes for determining minerals, and concludes that the best scheme should regard the physical properties as *suggestive* before, and *confirmatory* after, the chemical composition, the true *determinative* factor, has been ascertained. By his scheme, the following is the order of tests. (1.) Test metallic and malleable minerals, for metals. (2.) Test specifically light and black minerals, for hydrocarbons. (3.) Test minerals having any taste, for salts. (4.) Test minerals with metallic, adamantine, and resinous lustre, in open tube and otherwise, for sulphur, arsenic, antimony, selenium, tellurium. (5.) Test other minerals for silica, and then test as required, (6) for phosphates and borates, (7) for carbonates, (8) for sulphates, (9) for volatile acids. (10.) Then try open tube tests. (11.) Bead tests for weak acids, chromium, vanadium, &c. (12.) Blowpipe tests. 10, 11 and 12, in some cases, would probably be done in test 4. D. A. L.

Experimental Petrogeny. By KARL B. SCHMUTZ (*Jahrb. f. Min.*, 1897, ii, 124—155).—A summary of this paper has already been given by Doelter (*Abstr.*, 1897, ii, 54; compare also *Abstr.*, 1897, ii, 329). L. J. S.

Amber. By PAUL DAHMS (*Jahrb. f. Min.*, 1897, ii, Ref., 273—274; from *Schriften naturforsch. Ges. Danzig*, 1897, 9, 1—19).—The commercial clarification of cloudy amber by heating in oil depends on the pores of the amber becoming filled with oil. Mineral and albuminous matters are extracted from the amber, and a little phosphoric acid is taken up from the crude oil. According to the author's determinations, amber contains.

- (a) A resin soluble in alcohol, with melting point 105°.
- (b) A resin soluble in ether, but insoluble in alcohol, m. p. 146°.
- (c) A resin soluble in alcoholic potash, m. p. 175°.
- (d) Succinin, 44—60 per cent.
- (e) Succinic acid, 3·2—8·2 per cent.

The soluble portion represents the original balsam of the amber tree, and the succinin is an alteration product of this. In the dry clarification of amber, by heating it in sand for some time, the soluble resins

melt and fill the pores ; the same result is brought about at the ordinary temperature after a long interval of time. L. J. S.

Minerals from Netherseal Colliery, Leicestershire. [Blende, Ankerite, Galena.] By GEORGE J. BINNS and GEORGE HARROW (*Trans. Fed. Inst. Mining Eng.*, 1897, 13, 252—255).—The following minerals are found in the coal-measures at Netherseal Colliery, Leicestershire.

Blende, as small, black crystals, lining cracks in bands and nodules of clay-ironstone, gave on analysis

Zn.	Fe.	Ca.	Mg.	Cd.	S.	Total.
63·20	2·11	0·50	0·36	trace?	33·91	100·08

Ankerite occurs as indistinct rhombohedra, associated with the blende, and also with galena ; it is white, but changes to buff on exposure to the air ; analysis gave

CaCO ₃ .	FeCO ₃ .	MgCO ₃ .	Gangue.	Total.
53·0	23·3	20·8	1·1	98·2

Galena, from clay filling a fault-fissure, gave

PbS.	FeS.	ZnS.	Gangue.	Total.	Sp. gr.
98·42	0·27	0·41	0·46	99·56	7·39

Hartley and Ramáge have detected copper, silver, iron, sodium, and potassium in this galena by spectroscopic methods.

Barytes, calcite, and copper pyrites are also found. L. J. S.

Minerals of the Harz. [Blende, Stibnite, Jamesonite, Orthite, Axinite.] By OTTO LUEDECKE (*Zeit. Kryst. Min.*, 1897, 29, 176—192).—The author here recapitulates all the original matter contained in his recent book, *Die Minerale des Harzes* (Berlin, 1896) ; this deals mainly with occurrences and crystallographic determinations. The following new analyses are given.

Blende from Clausthal gave, on analysis by Reinicke,

Zn.	Fe.	Pb.	S.	SiO ₂
64·25	2·25	0·03	33·13	0·51

This gives the ratio (Zn,Fe,Pb) : S = 1 : 0·9.

Stibnite from Wolfsberg was found to contain nothing but antimony and sulphur. It would, therefore, be useful for the determination of the atomic weight of antimony.

Jamesonite, in compact, felty masses of capillary crystals, from Schwenda gave, on analysis by G. Baumert,

Pb.	Sb.	S.	Fe.
49·57	28·53	19·84	0·53

Orthite, in crystals, from quartz veins in gabbro at Bärenstein, gave

SiO ₂ .	CaO.	MgO.	(Ce,La,Di) ₂ O ₃ .	(Al,Mn,Fe) ₂ O ₃ .	Sp. gr.
29·05	5·67	0·52	21·56	29·29	3·784

Axinite, in crystals, from crystalline limestone at Radauthal, gave Baumert results agreeing with the formula $H_4R''_{20}Si_{11}O_{44}, R'''_{12}Si_9O_{36}$.

SiO ₂ .	CaO.	FeO.	MgO.	MnO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	B ₂ O ₃ .	K ₂ O.	H ₂ O.
39·26	29·70	3·65	1·81	2·80	2·62	14·46	4·91	0·25	1·22

L. J. S.

Identity of Chalcostibite (Wolfsbergite) and Guejarite. By SAMUEL L. PENFIELD and AUGUST FRENZEL (*Amer. Journ. Sci.*, 1897, 4, 27—35; and *Zeit. Kryst. Min.*, 1897, 28, 598).—Chalcostibite was first described, from Wolfsberg, in the Harz, in 1835, as being orthorhombic and having the composition $\text{Cu}_2\text{S}, \text{Sb}_2\text{S}_3$. In 1879, Cumenge (Abstr., 1881, 517) gave the name guejarite to an orthorhombic mineral from Güejar-Sierra, Spain, which had, according to his analysis (I), the composition $\text{Cu}_2\text{S}, 2\text{Sb}_2\text{S}_3$. The later crystallographic determinations made by Laspeyres (Abstr., 1892, 124) on the Wolfsberg mineral agreed completely with those previously obtained for guejarite; and from a re-examination of Cumenge's original material, the present authors have established the identity of chalcostibite and guejarite which was suggested by this agreement. Analyses by Frenzel, made on measured crystals of "guejarite," gave the results under II, III, and IV, these agreeing closely with the formula $\text{Cu}_2\text{S}, \text{Sb}_2\text{S}_3$, the percentage composition of which is given under VI. For these analyses, every crystal was first qualitatively tested for copper, in order to make certain that no stibnite crystals were present, since this mineral, as noticed by Cumenge himself, closely resembles chalcostibite in colour, lustre, the perfect pinacoidal cleavage, and in crystal habit. The excess of antimony in Cumenge's analysis (I) was probably due to the presence of stibnite.

	I.	II.	III.	IV.	V.	VI.
S	25·0	26·28	—	26·12	26·20	25·87
Sb	58·5	48·86	48·50	48·44	48·45	48·50
Cu	15·5	24·44	25·92	25·23	24·72	25·63
Pb	trace	0·58	—	0·32	—	—
Fe	0·5	0·42	—	0·49	—	—
Zn	—	—	—	0·18	—	—
	<hr/> 99·5	<hr/> 100·58		<hr/> 100·78	<hr/> 99·37	<hr/> 100·00
Sp. gr....	5·03	4·96				

Chalcostibite has recently been found at the Pulacayo mine, Huanchaca, Bolivia, where it occurs with tetrahedrite, pyrites, and quartz. Analysis of crystals gave the results under V (Frenzel). These crystals, being very perfect and rich in terminal planes, have enabled accurate determinations of the crystallographic constants of chalcostibite to be made; Penfield finds $a:b:c = 0·5312:1:0·63955$, the perfect cleavage being taken as parallel to the basal plane, and the elongated striated zone as the macroaxis b .

L. J. S.

[Bournonite from Bolivia.] By AUGUST FRENZEL (*Zeit. Kryst. Min.*, 1897, 28, 607—609).—The veins of the Pulacayo silver mine, at Huanchaca, are in a trachytic quartz-porphry, and contain the following minerals: quartz, pyrites, tetrahedrite, blende, galena, copper pyrites, rarely stibnite, stephanite, chalcostibite (preceding abstract), and bournonite, together with traces of bismuth and tin compounds. Tetrahedrite is the principal ore; it contains up to 10 per cent. of

silver. Bournonite occurs as small, bright, columnar crystals, sometimes embedded in the tetrahedrite; analysis gave

Pb.	Cu.	Ag.	Fe.	Zn.	Sb.	S.	Total.
40.88	12.70	trace	0.40	0.14	24.78	20.50	99.40
L. J. S.							

Composition of some Tellurium Minerals. By WILHELM MUTHMANN and E. SCHRÖDER (*Zeit. Kryst. Min.*, 1897, 29, 140—145).—The authors have examined specimens of tetradymite with the idea of determining the amount of selenium which has been shown by several previous analyses to be present in traces. Full details of the methods of analysis are given in the paper. Tetradymite from Orawicza, Hungary, gave I and II, after deducting about 11 per cent. of gangue; it occurs as greyish-white scales with copper pyrites and tetrahedrite in calcite; selenium is absent. Tetradymite in distinct crystals from Schubkau, Hungary, gave III, IV, and V; sp. gr. 7.0946; traces of selenium are present. All these analyses agree with the formula $2\text{Bi}_2\text{Te}_3, \text{Bi}_2\text{S}_3 = \text{Bi}_2\text{Te}_2\text{S}$.

	I.	II.	III.	IV.	V.	VI.	VII.
S	4.51	4.47	4.20	4.35	4.39	9.31	9.40
Bi	58.93	59.34	60.36	59.98	60.34	79.31	78.82
Te	35.30	35.56	35.25	35.35	35.68	12.82	12.66
	<hr/> 98.74	<hr/> 99.37	<hr/> 99.81	<hr/> 99.68	<hr/> 100.41	<hr/> 101.44	<hr/> 100.88

A tellurium mineral from Cumberland, analysed by Rammelsberg in 1853, gave VI and VII, corresponding with the formula $\text{Bi}_4\text{S}_3\text{Te}$ or $\text{Bi}(\text{S}, \text{Te})$. The irregular masses are grey in colour with a metallic lustre, and have a perfect cleavage in one direction. On the cleavage surface, there are cracks intersecting at 60° , and the thermal conductivity figure is a circle, so that the crystal system is rhombohedral as in tetradymite. Sp. gr. 7.321. The formula, in which bismuth is bivalent, is analogous to that of karelinite ($\text{Bi}_4\text{O}_3\text{S}$). This new mineral is named *grünlingite*.
L. J. S.

[Cubic Ferric Oxide] from Stromboli. By ALFRED BERGEAT (*Jahrb. f. Min.*, 1897, ii, 109—123).—The older lavas of the volcanic island of Stromboli, in the Lipari Islands, are andesites, whilst the newer are basaltic in character. A leucite rock, namely, leucite-basanite, is described. Good mineral specimens are rare on the island; besides augite crystals and thin plates of hæmatite, only the following is described.

The mineral, of which the following analysis by Hilgenstock is given, occurs as dull crusts of a dark, blue-grey colour on lava. This crust is composed of small, regular octahedra, often arranged in groups parallel to a cubic axis, and then having the appearance of tetragonal prisms terminated by pyramids. The mineral resembles hæmatite in the colour of the powder, but differs from it in being strongly magnetic. The sp. gr. of the crystals is 4.998, and of the powder, after separating tridymite and plagioclase, 5.247. On fractures, and in thin

sections, the crystals are seen to enclose much hæmatite as thin plates arranged parallel to the octahedral faces.

Fe ₂ O ₃ .	FeO.	MgO. MnO.	Al ₂ O ₃ (probably from plagioclase).	Gangue.	Total.
94·68	2·67	0·17	0·25	1·48	99·25

This description suggests martite, but the author is inclined to regard the mineral as magnesoferrite (MgO, Fe₂O₃) enclosing much hæmatite. L. J. S.

Precious Stones of New South Wales. By J. MILNE CURRAN (*Journ. and Proc. Roy. Soc. N.S.W.*, 1897, 30 (for 1896), 214—285).—In this paper, which is illustrated by eight plates, the modes of occurrence and characters of all the known precious stones from New South Wales are described. A complete bibliography and historical sketch are added, together with some methods for the discrimination of rough stones.

Diamond is found in the drift at three localities, the most important being Bingara.

Sapphire chiefly occurs in the tin-bearing drifts of the Emmaville and Tingha districts; it has also been found in basalt. Ruby is very rare in the colony.

Emerald occurs near Emmaville in a decomposed felsitic matrix associated with topaz, fluorite, mispickel, cassiterite, &c. Transparent crystals gave, on analysis by J. Petrie,

SiO ₂ .	Al ₂ O ₃ .	BeO.	CaO.	MgO.	Na ₂ O.	H ₂ O.	Total.	Sp. gr.
65·20	17·80	14·40	1·00	0·64	0·34	0·62	100·00	2·73

Rare alkalis could not be detected spectroscopically.

Topaz is abundant in the tin-bearing drifts and granites of the northern part of the colony. Analysis of bluish-white, transparent material from Emmaville gave,

SiO ₂ .	Al ₂ O ₃ .	CaO.	F.	Total (less O for F).	Sp. gr.
30·29	60·90	0·40	15·05	100·30	3·50

Garnet is common, but good stones are rare. Red pyrope (anal. I) occurs near Bingara in a basic, holocrystalline, granular rock (anal. II) composed of pyroxene and felspar; the garnet is surrounded by a kelyphite border.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O, Na ₂ O.	H ₂ O.	Total.	Sp. gr.
I.	39·57	23·68	0·18	10·04	3·76	8·76	14·45	—	—	100·44	3·743
II.	42·4	18·4	10·4	—	trace	16·6	8·5	2·5	1·2	100·0	3·1
III.	49·80	9·90	8·64	—	—	15·80	15·86	—	—	100·00	—

Anal. III is of large phenocrysts of augite from an olivine-basalt dyke containing garnets, from near Harden.

Turquoise occurs as thin crusts and concretionary masses in a dark, carbonaceous shale, containing pyrites, from near Bodalla. It is of a good sky-blue colour, but on exposure becomes greenish owing to loss of water. Analysis gave,

P ₂ O ₅ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	CuO.	SiO ₂ .	H ₂ O.	Total.	Sp. gr.
31·90	36·236	1·264	1·70	7·45	0·50	21·00	100·05	2·67

Opal is well known from White Cliffs, where it occurs in Upper Cretaceous sandstones; the silica has been derived from beds of organic (diatomaceous and radiolarian) origin.

Zircon, beryl, nephrite, cordierite, serpentine, malachite, and various varieties of quartz are also described. L. J. S.

Pseudogaylussite from Holland. By F. J. P. VAN CALKER *Zeit. Kryst. Min.*, 1897, 28, 556—572).—Spheroidal groups of crystals, closely resembling the well-known pseudomorphs from Sangerhausen, in Thuringia, and other localities, have been found embedded in alluvial clay at Onderdendam in the province Groningen. The pyramidal crystals are of a yellowish colour, and the surfaces are rough and curved; in the interior, they show a cellular aggregate of differently orientated calcite grains. Analysis shows the presence of 89·9462 per cent. of calcium carbonate.

CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	Na ₂ O.	K ₂ O.
50·6281	0·5000	1·8657	1·2985	0·2718	0·1086
SiO ₂ .	CO ₂ .	SO ₃ .	Insol. (clay).	H ₂ O (at 100°). (on ignition).	H ₂ O Total.
0·1426	40·4659	0·3689	2·3804	0·7704	1·8011
					100·6020

Pseudogaylussite is also recorded from Kwadyk and Friesland in Holland.

A review of the literature of these pseudomorphs is given, and the evidence supplied by the chemical composition and external form discussed. No definite conclusion is arrived at as to what was the original mineral, which has been variously assumed to be gaylussite (Breithaupt, 1836), celestite (Des Cloizeaux, 1843), gypsum (Kenngott, 1870), anhydrite (Groth, 1878), and a hypothetical tetragonal chloro-carbonate of calcium (Dana, 1884). The author has failed to detect strontium by spectroscopic methods; and the presence of a little sodium carbonate and the porous structure of the pseudomorphs seem to suggest that gaylussite was the original mineral. Several measured angles are given, but, owing to the roughness and curvature of the faces, the variations are considerable, and they compare equally well with both gaylussite and celestite. L. J. S.

[Pyromorphite, Mimetite, &c.] from Broken Hill, N.S.W. By CHARLES W. MARSH (*Trans. Australian Inst. Mining Eng.*, 1897, 4, 138—159).—*Cerussite* is remarkable for the variety of crystalline aggregates produced by twinning.

Pyromorphite, occurring in crystalline aggregates, gave analyses I—III. A lemon- to orange-yellow variety called “chromo-phosphate” contains some chromic acid as well as arsenic.

	PbO.	P ₂ O ₅ .	As ₂ O ₅ .	V ₂ O ₅ .	Cl.	Total.
I. Brown	81·9	14·4	0·8	—	1·9	99·0
II. White	80·8	14·6	2·3	—	2·2	99·9
III. Straw-yellow.....	79·3	13·2	6·2	—	1·1	99·8
IV. Yellow	74·7	1·2	21·4	—	2·8	100·1
V. White	74·2	5·7	17·6	—	2·4	99·9
VI. Red	73·9	1·8	18·2	3·6	2·1	99·6

Mimetite crystals gave analyses IV—VI. The bright yellow is the most pure, sometimes containing only a trace of phosphoric acid; the lighter coloured and greenish specimens contain more phosphoric acid, whilst those coloured red and brown contain vanadium and graduate into vanadinite.

Wulfenite occurs as orange-yellow, orange-red, and deep red crystals, the last containing some chromic acid.

Stolzite occurs as smoky-grey, yellowish, and reddish tetragonal crystals, and in long, thin plates. [The last, of which figures are given, is probably identical with raspite (this vol., ii, 32)].

Several rare minerals are also mentioned as occurring at Broken Hill: namely, hedyphane, phosgenite, lanarkite, leadhillite, matlockite, percyllite, linarite, minium, jordanite, sartorite, boulangerite, and jamesonite. Anglesite and galena are also described. L. J. S.

Gypsum Deposits of Nottinghamshire. By ARTHUR T. METCALFE (*Trans. Fed. Inst. Mining Engineers*, 1896, 12, 107—114).—Bands of gypsum are abundant in the upper marls of the Keuper beds of Nottinghamshire and Derbyshire; it is worked as an ornamental stone, and for the manufacture of plaster of Paris. The composition of an ordinary sample is,

CaSO ₄ .	CaCO ₃ .	Oxide of iron.	Siliceous matter.	H ₂ O.	Total.
77·37	0·83	0·50	0·30	21·00	100·00

Anhydrite sometimes occurs in the centre of masses of gypsum.

L. J. S.

[**Analysis of Soda-mica**]. By FRANZ EIGEL (*Zeit. Kryst. Min.*, 1897, 29, 169; from *Jahresber. des F. B. Gymnasiums am Seckauer Diöcesan-Knabenseminar*, for 1894—5).—White mica from a “sericite-mica-schist” consisting essentially of quartz and mica, from near Pöllau, Styria, gave, on analysis,

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
51·43	32·11	trace	11·80	1·29	5·67	102·30

The optic axial angle is large. The amount of soda is much higher than shown in any previous analysis.

L. J. S.

Composition of Comendite. By SOLIMANN BERTOLIO (*Jahrb. f. Min.*, 1897, ii, Ref. 292; from *Rend. R. Accad. Lincei*, 1896, [v], 5, (2), 150—152. Compare Abstr., 1897, ii, 55).—The ægirite-liparite from S. Pietro in Sardinia has been called comendite; a specimen richer in alkalis, and with less quartz than usual, gave analysis I. Sp. gr. 2·57. Some of the felspar is schillerised, but still clear; analysis II shows it to be anorthoclase; sp. gr. 2·58—2·59. The amphibole, which resembles arfvedsonite, gave III; sp. gr. 3·33.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.
I.	68·5	14·5	1·0	3·0	—	trace	0·1	3·0	9·2	99·3
II.	66·1	18·2	trace	—	—	0·1	—	3·5	11·4	99·3
III.	49·10	5·50	4·20	27·70	0·50	0·13	0·17	1·60	10·50	99·40

L. J. S.

Sodalite-trachyte from the Siebengebirge. By WILLY BRUHNS (*Verh. naturhist. Ver. Bonn*, 1896, **35**, 39—56).—The peculiar rock from Kùhlsbrunnen, in the Siebengebirge, has often been described and is usually called an *agirite-trachyte*; it is now shown to contain sodalite, to which the cellular structure of the weathered rock is due. In the fresh rock, the sodalite is present in clear, colourless, isotropic grains; it dissolves easily in dilute nitric acid, yielding a clear solution, without any separation of gelatinous silica. The portion of the rock soluble in dilute acid gave analysis I; besides sodalite, this would only include a little glass and magnetite. A partial analysis (II) of the augite needles confirms the reference, made on optical grounds, to *agirite*. The felspar is all *sanidine*; magnetite is abundant, and a glassy base is rare; analysis of the fresh rock gave the results under III.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Cl.	Loss on ignition.	Total.
I.	34·2	31·2	trace	—	—	nil.	nil.	nil.	27·9	7·5	—	100·8
II.	—	2	28	not det.	—	little	—	nil.	10	—	—	—
III.	63·61	16·34	4·30	2·08	trace	1·42	0·37	5·54	6·21	0·18	0·77	100·82

Detailed descriptions and analyses are given of trachytes from other localities, which were examined on account of their similarity in appearance to the Kùhlsbrunnen rock; no sodalite was, however, found in these.

L. J. S.

Contact-metamorphism of Phyllites. By K. DALMER (*Jahrb. f. Min.*, 1897, ii, 156—158).—At Schneeberg, in Saxony, a phyllite composed of 24·93 per cent. of chlorite and 75·07 of muscovite has been altered into a rock containing andalusite 31·1, muscovite and biotite 68·9 per cent.; the two rocks, as shown by analyses I and II respectively, have essentially the same composition.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.
I.	39·49	34·47	5·86	5·74	1·85	0·25	5·38	1·17	5·78
II.	39·00	34·85	6·18	6·15	2·09	0·46	6·18	1·67	3·47

In this change, as represented by the following equation, part of the muscovite of the phyllite has been altered to andalusite, and the potassium silicate and silica so liberated have, with chlorite, formed biotite; $40\text{SiO}_2, 20\text{R}_2\text{O}_3, 2\text{RO}, 4\text{K}_2\text{O}, 2\text{Na}_2\text{O}, 12\text{H}_2\text{O}$ (muscovite) + $6\text{SiO}_2, 6\text{R}_2\text{O}_3, 8\text{RO}, 10\text{H}_2\text{O}$ (chlorite) = $12\text{Al}_2\text{SiO}_5$ (andalusite) + $18\text{SiO}_2, 6\text{R}_2\text{O}_3, 10\text{RO}, 3\text{K}_2\text{O}, 3\text{H}_2\text{O}$ (biotite) + $16\text{SiO}_2, 8\text{R}_2\text{O}_3, 3(\text{Na}, \text{K})_2\text{O}, 5\text{H}_2\text{O}$ (potash-soda mica) + $14\text{H}_2\text{O}$.

At Rothschenberg, in Saxony, a phyllite is altered into a rock composed of muscovite, biotite, and quartz; analyses show the presence of more free silica in the phyllite than in the altered rock, so that here biotite has been produced from chlorite and quartz, the potassium having been supplied by the muscovite. From chlorite or muscovite with quartz, cordierite may be produced.

L. J. S.

Meteoric Iron. By EMIL W. COHEN (*Ann. k. k. naturhist. Hof-museums Wien*, 1897, **12**, 42—62).—New analyses of the Nenntmannsdorf (Saxony), Lion River (S. Africa), Prambanan (Java), and

Chesterville (S. Carolina) irons gave the results under I, II, III and IV respectively; these differ from previous analyses in showing the presence of cobalt. It is pointed out that in octahedral irons, as in Lion River and Prambanan, the amount of Ni + Co is 8—11 per cent.

The Zacatecas (Mexico) iron gave analysis V; in the hydrochloric acid residue, there is an undetermined phosphide of nickel containing a relatively large amount of copper and but little iron. The mineralogical composition of this iron is given as

Nickel-iron.	Schreiber-site.	Troilite.	Daubréé-lite.	Chromite and silicate.	Carbon.	Nickel phosphide?	Undet. residue.
94.34	3.54	0.26	0.10	0.21	0.03	1.08	0.44

A new analysis of rhabdite from the See-Läsgen iron (compare Abstr., 1897, ii, 57) gave VI, from which $(\text{Fe}, \text{Ni}, \text{Co}) : \text{P} = 3.109 : 1$.

The Bischtübe (Russia) iron has the mineralogical composition,

Nickel-iron.	Nickel-iron phosphide.	Carbon.	Chromite and silicate.	Undet. residue.
96.97	2.52	0.09	0.01	0.41

The schreibersite, together with a little rhabdite from this iron, gave analysis VII, agreeing with $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$, and the flexible plates of tænite gave VIII. The present results differ considerably from Kislakowsky's (Abstr., 1892, 418), who found 17.90 per cent. of olivine and anorthite.

A new analysis of cohenite from the Wichita Co. (Texas) iron gave, after deducting about 8 per cent. of schreibersite, the results under IX, agreeing with the formula $(\text{Co}, \text{Ni}, \text{Fe})_3\text{C}$; the variations shown in previous analyses are to be explained by the presence of tænite.

An iron carbide from the telluric iron of Ævifak (Greenland) gave analysis X, showing it to be probably identical with the meteoric cohenite.

	Fe.	Ni.	Co.	P.	C.	Cr.	S.	Insol.	Total.	Sp. gr.
I.	94.33	5.48	0.71	0.29	—	nil.	—	—	100.81	7.8241
II.	92.06	7.79	0.69	0.05	—	—	—	—	100.59	—
III.	90.03	9.39	0.97	0.16	—	—	—	—	100.55	—
IV.	93.15	5.82	0.73	0.34	—	—	—	—	100.04	7.8738
V.	92.09	5.98	0.91	1.02	—	0.74	0.18	0.04	100.96	—
VI.	46.32	38.06	0.94	14.89	—	nil.	—	0.94	101.15	—
VII.	66.19	18.47	0.43	15.88	—	—	—	0.07	100.74	—
VIII.	62.19	35.90	0.35	0.92	0.75	—	—	—	100.11	—
IX.	90.80	2.37	0.16	—	6.67	—	—	—	100.00	7.3236
X.	92.73	0.95	0.39	—	5.93	—	—	—	100.00	—

L. J. S.

Physiological Chemistry.

Metabolism during Muscular Work in Dogs. By NATHAN ZUNTZ (*Pflüger's Archiv.*, 1897, 68, 191—211).—All mammals hitherto investigated need, in normal work, nearly the same amount of chemical energy per work unit, somewhat more than a third of the available

energy appearing as external work, whilst the remainder is changed into heat. In pulling work, the useful effect of the transformed energy is somewhat smaller than in climbing, and diminishes with increase of work. The horizontal movements of the animal's own body require, for equal weights moved through the same distance, so much the more work the smaller the animal is. The relationship between the work and the transformation of energy is nearly proportional to the superficial area of the body.

W. D. H.

Solubility of Paracasein in Artificial Gastric Juice. By W. LINDEMANN (*Virchow's Archiv.*, 1897, 149, 51—65).—Previous researches on caseinogen (here called casein) have shown that the residue obtained on gastric digestion is small, and with excess of gastric juice is absent (Salkowski).

In the present investigation, casein (here called paracasein) was employed, and the powdered proteid subjected to the action of gastric juice (in some experiments, however, it was previously dissolved in a minimal quantity of alkali); a residue was found in all cases, varying from 0.12 to 10.07 of the substance taken, but the percentage usually obtained was 3 or 4. Casein is, therefore, less digestible than caseinogen; the residue is smaller the larger the amount of digesting fluid employed; the quantity of acid in the mixture has some influence, but the duration of the digestion beyond 24 hours has none.

W. D. H.

Origin of Fat from Proteid. By EDUARD PFLÜGER (*Pflüger's Archiv.*, 1897, 68, 176—190).—A further polemical contribution to a much discussed subject; the author does not believe in the origin of fat from proteid, and seeks to show from the experiments of those workers who do believe in it, that their conclusions are incorrect.

W. D. H.

Fat of Muscle: Estimation of Fat in Animal Substances. By ELLY BOGDANOW (*Pflüger's Archiv.*, 1897, 68, 408—430; 431—433).—The principal point made out is that, in the later extractions of muscle with ether, the fat obtained is different from that obtained in the first extracts, and that the fat obtained last is very rich in free fatty acids; this confirms the observations of Dormeyer, who used an entirely different method. The method here used is explained at full length, with wood-cuts of the apparatus employed.

Extraction of animal tissues with ether does not, however, extract all the fat; more goes into solution on subsequent extraction with boiling 90 per cent. alcohol. The largest yield is obtained by a five days extraction with alcohol in a Soxhlet's apparatus, after the finely divided material has been allowed to remain a day under ether. The experiments in this direction are not complete, but it is hoped that this simple method will give results equally trustworthy with those obtained by Dormeyer's more complicated process.

W. D. H.

Biological History of Phosphates. By LÉOPOLD JOLLY (*Compt. rend.*, 1897, 125, 538—539).—The ordinary molybdic acid solution in dilute nitric acid serves for the detection of phosphates in animal tissues, to which, if they contain phosphoric acid or its salts, a yellow colour is imparted. No similar coloration is produced by macerating

the same tissues with nitric acid of the same strength. The author's observations show that many tissues, even after being macerated for some time with dilute acetic acid or dilute nitric acid, retain phosphoric acid which can be detected by means of the molybdc reagent in the manner indicated. It follows that the association of the tissues with this part of the phosphoric acid must be of a very intimate character.

C. H. B.

Catechol-like Substance in the Suprarenal Capsules. By OTTO VON FÜRTH (*Zeit. physiol. Chem.*, 1897, 24, 142—158).—This paper gives an account of attempts to isolate the substance which has been known since Vulpian's researches to exist in the medulla of the suprarenal capsules and gives a greenish colour with ferric chloride. The author does not appear to have been any more successful in these attempts than his predecessors; he describes the material as catechol-like, but admits that it contains nitrogen.

W. D. H.

The Organic Ground Substance of Fish Scales. By CARL THORE (GRAF) MÖRNER (*Zeit. physiol. Chem.*, 1897, 24, 125—137).—The scales of various fishes were investigated, and the organic ground substance was found to be not wholly composed of collagen, about a fifth of it consisting of another albuminoid named *ichthyolepidin*, which differs from collagen in containing loosely united sulphur, from keratin in its small percentage of sulphur (1·09), and from elastin by its smaller resistance to chemical reagents.

W. D. H.

Composition of Sow's Milk, with Special Regard to the Amount of Fat. By M. PETERSEN and FR. OETKEN (*Bied. Centr.*, 1897, 711—712; from *Milchzeit.*, 1896, 665).—The examination of seventeen samples of sow's milk, from Oldenburg, and of a few other samples, showed that the amounts of fat and dry matter are greater than in cow's milk. The following percentage results are given. Fat, 2·4 to 12·1; dry matter (average of four samples), 20·4; proteids, 3·8 to 5·3; sp. gr. (one sample only) = 1·0128. The high percentage of fat (average of 22 samples = 6·6) is in accordance with previous results.

N. H. J. M.

Physiological Action of Tannin and Gallic Acid. By ERICH HARNACK (*Zeit. physiol. Chem.*, 1897, 24, 115—124).—By administering to men or dogs small, medicinal doses of tannin or gallic acid, the quantity of gallic acid in the urine is very small, but the greater amount is contained in the fæces. It is probable that some of the gallic acid which passes into the urine is decomposed, and traces of pyrogallol are found, if, in searching for it, the acidified urine has been evaporated; if the evaporation is omitted, pyrogallol is never found. Pyrogallol is highly poisonous, and is not formed in the organism.

On giving larger doses of gallic acid, more passes into the urine, especially if alkalis are given as well.

By feeding on free tannin, none passes into the urine; but it is found after giving a freshly-prepared solution of tannin in alkali. For the isolation of tannin, the salting-out method by saturated sodium chloride solution, and precipitation by solution of gelatin or albumin

free from globulin, is recommended. The separation of small quantities of pyrogallol and gallic acid is only possible when the solubility of the former in boiling benzene is made use of. W. D. H.

[Physiological Action of Naphthalene.] By THEO. KLINGMAN (*Virchow's Archiv.*, 1897, 149, 12—22).—A number of previous workers have noticed that the most marked effect of the administration of naphthalene is an opacity of the lens and other degenerative changes in the eye-ball. In the present research on rabbits, naphthalene dissolved in liquid paraffin was given by the stomach; in the urine, phenol was found corresponding to about a tenth of the naphthalene given. The animals were killed at varying intervals; in the early stages, an irido-cyclitis was found, which is believed to be the starting point of the subsequent eye-changes in the cornea, lens, and retina. The primary lesion is not in the retina, as Panas considered. W. D. H.

Physiological Action of Eucaïne B. (4-Benzoyloxy-trans-2:2:6-trimethylpiperidine). By GAETANO VINCI (*Virchow's Archiv.*, 1897, 149, 217—235).—The action of eucaïne B. (4-benzoyloxy-trans-2:2:6-trimethylpiperidine) is similar to that of eucaïne, previously described (*ibid.*, 145), and of cocaine. Locally, it dilates the blood-vessels, although in smaller measure than does eucaïne, and it also enlarges the pupil. Anæsthesia is produced, as with cocaine and eucaïne, by direct contact with the sensory nerve-endings. There is an action on the central nervous system, and a curare-like paralysis of the motor and vagus nerve-endings; this is attributed to the absence of the COOH group, and is not observed with eucaïne and cocaine, which contain that group. Eucaïne B has an antiseptic action; it is less soluble than the other drugs, but is cheaper and an equally good local anæsthetic. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nature of Fermentative Changes in Natural and Polluted Waters, and in Artificial Solutions, as Indicated by the Composition of the Dissolved Gases. Part IV. Humus: Its Formation and Influence in Nitrification. By WALTER E. ADENEY (*Trans. Roy. Dublin Soc.*, 1897, [ii], 6, 269—281. Compare Abstr., 1896, ii, 322).—The author gives reasons for adopting the terms, carbon oxidation and nitrogen oxidation or nitrification, to respectively denote the two stages by which organic substances successively undergo complete aërobic bacterial fermentation in waters. With the adoption of these terms, the author proposes the classification of all fermentable substances into (1) carbon-oxidisable substances, or all fermentable organic substances which have not undergone carbon-oxidation; and (2) nitrifiable substances, or ammonium compounds, and organic compounds which have suffered carbon-oxidation.

The author has described the changes which result from these two

stages of fermentation, in his previous communication. The object of the experiments now recorded has been to ascertain the fermentative properties of the humus of ordinary cultivated soils, and thereby to complete the information already published (*loc. cit.*) on the fermentative properties of the nitrifiable organic substances which are to be found in natural waters.

The humus employed in these experiments was obtained from a large heap of wet refuse matter, which consisted of the solid matters that had been separated from sewage and mixed with freshly precipitated manganese peroxide in about equal proportions. The heap was allowed to ferment for about three months, at the expiration of which time the peroxide was found to be completely reduced and converted into manganese carbonate. The organic matters, which at this time amounted to about 8 per cent. of the air-dried mass, were also found to have undergone a practically complete first-stage fermentation or carbon oxidation, and to have all the properties of the humus of ordinary cultivated soil.

That the reduction of the peroxide to carbonate of manganese can be brought about by bacterial fermentation, has been shown by McWeeney, who found that, when freshly precipitated manganese peroxide was kept in sterilised liquid media, it remained unchanged, but that when the same media were seeded with small pieces of the fermented refuse matters above referred to, a rapid and abundant growth of living organisms ensued, and the complete reduction of the peroxide to carbonate quickly followed.

The author records a number of experiments with this humus, which show that it possesses fermentative properties similar to those which he has already shown peaty colouring matters and fermented organic matters to possess, the most characteristic property of which is to determine the *nitric* fermentation of ammonium compounds.

The possible changes which nitrifiable substances, to be met with in natural waters, may undergo are summarised as follows.

1. When the nitrifiable organic substances are freshly formed, and are present in comparatively large quantity in a water, the formation of a volume of carbonic anhydride, in proportion to the volume of oxygen consumed, and the formation also of a quantity of nitrous or of nitric acid, or of both, but in small quantities, may attend the earliest stage of fermentative change they may undergo.

2. At subsequent stages, the volume of carbonic anhydride formed is not so large, and the quantity of inorganic nitrogen products, nitrous or nitric acid, becomes more marked, in proportion to the oxygen consumed.

3. At a still later stage, at the completion of which all the ammonia becomes fermented, little or no carbonic anhydride may be formed, but, on the contrary, a little may become "fixed"; the inorganic nitrogen product consists then of nitric acid solely.

4. When little or no ammonia is present, freshly formed nitrifiable organic matters may undergo at first a slow change, during the first steps of which distinct amounts of carbonic anhydride and of oxygen may be formed and consumed, respectively; small quantities of nitric acid are formed at the same time.

5. But, after these earlier steps of change, the fermentation becomes

slower, and finally so slow as to be scarcely appreciable; still, the results are the formation of carbonic anhydride and nitric acid, and the consumption of a proportionately small volume of oxygen. W. E. A.

Fermentation Phenomena. By ALFRED STAVENHAGEN (*Ber.*, 1897, 30, 2422—2433).—A solution prepared from yeast by Buchner's method (*Abstr.*, 1897, ii, 154), but filtered through a Chamberland filter, was found to be perfectly sterile and possessed all the properties of that prepared by Buchner, except that it did not cause the slightest fermentation with cane-sugar, glucose, or milk-sugar. The author considers that the acknowledged presence of micro-organisms in the solution obtained by Buchner is sufficient to invalidate his experiments on the fermentation of sugar without yeast cells. A. H.

Chemical Characteristics of the Woody Matter of the Oak. By PAUL METZGER (*Bied. Centr.*, 1897, 26, 678—679; from *Inaug. Diss. Munich*, Heilbronn, 1896).—The sap-wood and heart-wood of oak both contain the same tannin, the composition of which agrees fairly well with Böttinger's formula, $C_{15}H_{16}O_{11}$. The tannin of the bark, however, seems to be present in a partly decomposed condition, and to contain phlobaphen. Both tannins must be considered as glucosides, as they are converted by boiling with dilute acids into phlobaphen, gallic acid, and glucose. Phlobaphen, $C_{33}H_{34}O_{13}$, is capable of taking up twelve acetyl groups.

Free gallic acid was found in the bark, sap-wood, and heart-wood of all ages. All three parts of the wood contain the same fats (the glycerol ethers of palmitic, stearic, cerotic, and oleic acids), oxalic, malic, and tartaric acids, cholesterol, cane-sugar, and pentosans. Starch occurs in the sap-wood and in the heart-wood, but not in the bark.

The amount of ash in the bark decreased from the root to the top, but increased in the sap-wood and heart-wood. The phosphoric acid in the bark increased towards the top, but diminished in the sap-wood and heart-wood; there was only an increase of phosphoric acid in the sap-wood of the newest shoots. Chlorine could not be detected in any of the ashes. N. H. J. M.

Effect of Humus on the Percentage of Nitrogen in Oats. By HARVEY W. WILEY (*Landw. Versuchs.-Stat.*, 1897, 49, 193—202).—A number of experiments, extending over three years, are described, in which oats were grown in large pots containing peaty soil, without manures and with a variety of manures. The soil contained, on the average, less than 10 per cent. of mineral matter, over 2.5 per cent. of nitrogen, and very little potash and phosphoric acid. The best of the soils employed was free from nitrifying organisms, but contained ammonia organisms in a fairly active condition.

The most striking result obtained was the high percentage of nitrogen in the produce, amounting to about 25 per cent. more than is found in oats grown on ordinary arable land. This increase is mainly in amide nitrogen and not in proteid nitrogen, and is, at least in part, due to direct absorption, from the soil, of nitrogenous matter which has

not been nitrified. The following average results show the total and amide nitrogen of the produce.

Grain and chaff.		Straw.		Roots.	
Total N.	N. as amides.	Total N.	N. as amides.	Total N.	N. as amides.
2.63	0.35	1.99	0.70	1.45	0.32

The amount of proteid nitrogen remained within the limits of the usual amounts obtained on ordinary soil.

Potash and nitrogenous manure, in the amounts applied, had no appreciable effect on the amount of produce. Phosphates raised the yield and, at the same time, lowered the percentage of nitrogen, probably owing to the increased crop rather than to any injurious action of the phosphates.

The three phosphatic manures employed (Florida phosphate, basic slag, and superphosphate) had almost the same effect on the amount of produce.

N. H. J. M.

Analytical Chemistry.

Use of the Electrometer as Indicator in the Titration of Acids and Bases. By WILHELM BÖTTGER (*Zeit. physikal. Chem.*, 1897, 24, 253—301).—Behrend (Abstr., 1893, ii, 387) has shown that an electrometer may be used to determine the end point in mercury titrations, a chain being employed of the type: mercury | mercurous nitrate | mercurous nitrate | mercury. The author shows that a similar method may be used in the titration of acids and bases, if a hydrogen electrode be employed, the form used by the author being made of gold electrolytically coated with palladium, the E. M. F. being determined by the aid of a capillary electrometer and a Clark or Weston normal cell. Titrations were made of solutions of hydrochloric, isobutyric, tartaric, phosphoric, arsenic, and carbonic acids, and of sodium hydroxide, aniline, ammonia, and a mixture of sodium hydroxide with benzylamine. The E. M. F. was found, after the addition of each c.c. of the neutralising liquid, and in a second experiment after each drop, in the neighbourhood of the point of neutralisation. Curves are constructed with the number of c.c. added as ordinates, and the E. M. F. as abscissæ. The form of the curve depends on the dissociation constant of the acid, but in all cases it ascends, at first slowly, then very rapidly, then again slowly, an almost vertical part indicating the neutral point. In all the cases considered, the form of the curve is the same as that obtained theoretically from the equation

$$\pi = 0.0002T \cdot \log C_2/C_1,$$

where C_2 and C_1 are the ion concentrations of the hydrogen, although the absolute values of the E. M. F. may not agree always with those obtained from the curve. For the weak acids, the method is also available, whilst with phosphoric and arsenic acids the points corresponding with the formation of the compounds NaH_2PO_4 and Na_2HPO_4 and the corresponding arsenic salts are indicated. With arsenious and boric acids, the point where one-third of the hydrogen is displaced

is seen on the curve. The availability of the method for weak organic acids is also proved, and the author points out that the agreement of the results with the theoretical deductions may be also taken as a further proof of the validity of the theory.

L. M. J.

Estimation of Perchlorate in Sodium Nitrate. By F. WINTERER (*Chem. Zeit.*, 1897, 21, 75—76).—Ten grams of the sample of "Chili saltpetre" is introduced into a tube containing 10 c.c. of fuming nitric acid and a little silver nitrate. The tube is then sealed and heated for 5 hours at 230°. The silver chloride thus formed is afterwards weighed.

Any chlorine existing as chloride or chlorate must be determined and allowed for.

L. DE K.

Separation of Bromine from Mixtures of Bromides and Chlorides. By HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1897, 125, 527—530).—When bromine is liberated from dissolved bromides by the action of cupric sulphate and potassium permanganate, the collection and direct estimation of the bromine is difficult. Distillation with water vapour is inconvenient, owing to the large volume of condensed liquid, but the bromine can readily be carried over in a current of air and absorbed in a dilute solution of an alkali. The salt to be analysed and the copper sulphate are dissolved in a flask with a neck 160 mm. long, and the permanganate is then added. The condenser tube and the tube carrying the current of air pass through a stopper which is ground into the neck of the flask. The alkali solution (3 or 5 per cent.) is contained in an inclined absorption tube consisting of a series of bulbs connected by short, narrow tubes and the absorption is complete even when 2250 c.c. of air per minute is passed through the liquid in the flask from a tube 3 mm. in diameter. The liquid in the flask may be heated by means of a water bath to any desired temperature, and, in order to compensate for evaporation, the air may first be saturated with water vapour by bubbling it through water contained in a flask heated in the same water bath.

When all the bromine has been expelled and absorbed, the liquid in the absorption tube is mixed with some sulphurous acid, then with silver nitrate solution, and finally with nitric acid in moderately large excess; the liquid is boiled for some time, and the precipitated silver salt dealt with in the usual way.

C. H. B.

Estimation of Sulphur in Iron. By OTTO HERTING (*Chem. Zeit.*, 1897, 21, 87).—The author states that the results obtained by Wiborgh's colorimetric process are untrustworthy, as the quantity directed to be taken for analysis is far too small. The best results are obtained by Wood's cadmium process, the sulphur in the cadmium precipitate being titrated by means of iodine.

De Koninck's proposal of adding a little stannous chloride when dissolving the sample in hydrochloric acid, so as to prevent oxidation of the hydrogen sulphide, is considered by the author to be superfluous, although it must be admitted that the action proceeds in a more steady and regular way (*Abstr.*, 1895, ii, 528).

L. DE K.

Estimation of Sulphur in Pyrites by means of Sodium Dioxide. By CHARLES GLASER (*Chem. Zeit.*, 1897, 21, 40—41).—When pyrites is oxidised by heating it with sodium dioxide, the melt,

on being treated with water, sometimes deposits a blackish powder which contains ferrous sulphide. The author now states that, in such a case, the experiment need not be rejected; it is only necessary to add a little more of the sodium dioxide to ensure complete oxidation.

When testing pyrites rich in sulphur, there is no necessity for rendering the silica insoluble before precipitating with barium chloride, but excess of the latter should be avoided. L. DE K.

Estimation of Mixed Sulphides, Sulphites, Sulphates, and Thiosulphates. By FRED W. RICHARDSON and HENRY E. AYKROYD (*J. Soc. Chem. Ind.*, 15, 171—173).—One portion of the solution is devoted to the estimation of sulphates, the neutral solution having been acidified with 5 grams of tartaric acid, is precipitated in the cold by barium chloride; the thiosulphates remain undecomposed, and the precipitate contains only some barium sulphate with some sulphite, the latter being removed by treatment with hot dilute hydrochloric acid and washing with hot water. From another portion of the solution, the sulphides are precipitated by ammoniacal zinc chloride. The filtrate from the zinc sulphide is then coloured with methyl-orange, and N/10 sulphuric acid run in until the change in the indicator shows that the sodium sulphite has been converted into sodium hydrogen sulphite. The mixture is now made up to a known volume and employed for titrating a measured quantity of N/10 iodine solution, after which the acidity developed is ascertained by titration with N/10 sodium hydroxide. In accordance with the equation $\text{NaHSO}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{NaHSO}_4 + 2\text{HI}$, each molecule of sodium sulphite originally present will require three molecules of sodium hydroxide to restore neutrality. The excess of iodine above that consumed by the sulphite is calculated into thiosulphate. The results obtained in analysing a solution of known composition were very close. M. J. S.

Estimation of Phosphorus in Iron and Steel. By OTTO HERTING (*Chem. Zeit.*, 1897, 21, 138—139).—The author did not get satisfactory results with Carnot's method of direct weighing of the molybdate precipitate; moreover, no better results were obtained with Mauermann's process, in which the precipitate is dissolved in standard ammonia and the excess titrated with standard acid, using corallin as indicator. A colorimetric method proposed by Namias, based on the blue coloration developed when dissolving the yellow precipitate in sodium thiosulphate, gives good results, but offers no special advantage over Emmerton's permanganate process.

The latter process has been slightly modified by the author. One gram of pig-iron is dissolved in 50 c.c. of nitric acid of 1.135 sp. gr., heated to boiling, and mixed with 20 c.c. of a solution of potassium permanganate (8 grams per litre); after boiling for 2 minutes, a saturated solution of ammonium oxalate is added drop by drop until the brown manganese precipitate has redissolved. After boiling for another 2 minutes, 5 c.c. of nitric acid of sp. gr. 1.42 is added, the liquid filtered, and the insoluble matter washed twice with hot water; as soon as the temperature has fallen to 65°, the liquid is poured into a beaker

containing 100 c.c. of molybdate solution, heated at 60°, and well stirred. The precipitation of the phosphoric acid is complete in 15 minutes; the bulk of the liquid is now poured off, and the precipitate washed on a filter with acid ammonium sulphate solution (10 grams ammonium sulphate, and 20 c.c. of sulphuric acid in 1 litre of water) until all the iron is removed. The precipitate is then dissolved off the filter by means of dilute ammonia, and filtered into an Erlenmeyer flask containing 10 grams of granulated zinc; dilute sulphuric acid (1:2) is added in excess, and the whole heated for 8 minutes. It is then filtered through a quick filter containing a few pieces of zinc, and the filtrate at once titrated with permanganate; the strength of the permanganate expressed in iron, multiplied by 0.0164, represents the phosphorus. When testing wrought iron or steel, 5 grams of the sample is dissolved in 90 c.c. of nitric acid of 1.135 sp. gr., and 10 c.c. acid of 1.42 sp. gr. is afterwards added. L. DH K.

Estimation of Citrate-Soluble Phosphoric Acid in Basic-Slags. By O. BÖTTCHER (*Chem. Zeit.*, 1897, 21, 168—169).—The author states that, if the solution of the basic-slag in Werner's ammonium citrate solution is mixed with a sufficiency of magnesium mixture and well agitated in a shaking apparatus for half an hour, the precipitation of the phosphoric acid is complete. If, however, the liquid is not then at once filtered, a gradual separation of silica will take place and the results will be untrustworthy. L. DE K.

Detection of Carbamic Acid. By PIERRE NOLF (*Zeit. physiol. Chem.*, 1897, 23, 505—520).—The author shows that “(1.) Normal ammonium carbonate, or a mixture of ammonium chloride and sodium carbonate, yields a considerable quantity of carbamic acid when treated by Drechsel's method. (2.) The same is true of ammonium hydrogen carbonate, or a mixture of pure sodium hydrogen carbonate and ammonium chloride. (3.) An aqueous solution of free carbonic acid and ammonium chloride gives a similar result. (4.) Instead of ammonium chloride, other ammonium salts can be used; for example, the nitrate, oxalate, or acetate.” Both dilute (1:600) and comparatively concentrated solutions were experimented with. The presence of carbamic acid was detected by shaking, preferably at 0°, first with a little lime, and again after adding calcium chloride; the liquid was now either filtered and sealed up in a glass tube, when the gradual appearance of a turbidity indicated the presence of calcium carbamate, or it was filtered into alcohol, the residue digested with ammonia, and the extract also filtered into alcohol, the precipitate that formed in the alcoholic liquid being examined after the lapse of half an hour, to see whether it had the characteristic form of calcium carbamate. It is concluded “that not only the reactions of carbamic acid, but calcium carbamate itself, will be obtained by Drechsel's method, wherever ammonium carbonate is present in solution, or free carbonic acid side by side with an ammonium salt.” A quantitative estimation is only possible when it is a solution of the calcium salt that is being dealt with; the amount of ammonium carbamate present in an alkaline solution is purely a matter of chemical equilibrium. C. F. B.

Estimation of Free Alkali and Alkali Carbonate in Soaps, with and without the use of Alcohol. By WILLIAM WALTKE (*Chem. Zeit.*, 1897, 21, 137).—The author states that soap should not be dried before extracting with alcohol, as the caustic alkali is then to a serious extent converted into carbonate by the carbonic anhydride from the air. Better results are obtained by dissolving 5 grams of the sample in 75 c.c. of absolute alcohol contained in an Erlenmeyer flask fitted with a soda-lime tube to prevent carbonic anhydride from entering the flask; after dissolution has been completed by the aid of a gentle heat, the liquid is filtered inside a water oven, the insoluble matter washed a few times with hot absolute alcohol, and the free alkali then titrated with N/10 sulphuric acid, using phenolphthalein as indicator. To estimate any alkali carbonate, the insoluble residue is dissolved in cold water, and also titrated with the acid, this time using methyl-orange as indicator.

The estimations may also be made without using alcohol. The free alkali can be estimated by dissolving 5 grams of the sample in 250 c.c. of hot water free from carbonic anhydride, and pouring this solution slowly into 100 c.c. of a 5 per cent. solution of barium chloride. The free alkali in the filtrate is then titrated as before. Another 5 grams of soap is then dissolved in 15 c.c. of water and nearly dried on a sand bath with constant stirring, passing a current of carbonic anhydride over the mass all the time. After drying at 110°, the residue is weighed to ascertain the amount of moisture; the carbonic anhydride is then estimated by means of a Geissler's apparatus, and after allowing for the amount absorbed by the free alkali, the difference is calculated into alkali carbonate.

L. DE K.

Estimation of Silver in Silver Plating Solutions. By T. J. BAKER (*Chem. News*, 1897, 76, 167).—Weighing the precipitate obtained with hydrochloric acid, also fusing the impure silver chloride with sodium carbonate and nitre, give unsatisfactory results; therefore, the author boils about 50 c.c. of the solution with a slight excess of nitric acid, filters, washes, and dries the precipitate, wraps it and the filter ash together in assay lead, and then cupels.

D. A. L.

Separate Estimation of Alumina and Iron Oxide in Phosphates. By F. LICHTSCHLAG (*Chem. Zeit.*, 1897, 21, 264—265).—Two grams of the sample is fused with 8 grams of sodium carbonate for 20 minutes, then quickly cooled, and the product, which can readily be detached from the platinum crucible, is put into a beaker, the crucible being rinsed with dilute hydrochloric acid, which is then used to dissolve the melt. When the latter is completely dissolved, the solution is neutralised in a 200 c.c. flask with aqueous soda, heated to boiling, 30 c.c. of a 20 per cent. solution of aqueous soda is added, and the whole heated for 15 minutes. When cold, the liquid is made up to the mark, and 75 c.c. is poured off through a quick filter; as soon as 50 c.c. has collected, it is mixed with excess of hydrochloric acid, a few drops of sodium phosphate solution are added, and, after boiling, the alumina is precipitated as phosphate by adding a very slight excess of ammonia.

The residue on the filter is dissolved in hydrochloric acid, which is

then added to the contents of the flask ; after adding some more acid, the liquid is introduced into a 500 c.c. flask and the iron reduced at 70° by means of zinc. When cold, the liquid is made up to the mark, and the titration proceeded with as Fresenius directs. L. DE K.

Estimation of Manganese in Steel and Iron. By LEOPOLD SCHNEIDER (*Chem. Zeit.*, 1897, 21, 41).—The sample is dissolved in nitric acid, and the solution, diluted with twice its volume of water, is boiled and mixed with pure lead peroxide, when the manganese is instantly oxidised to permanganic acid. After filtering through asbestos, the filtrate is titrated with a standard solution of hydrogen peroxide until colourless. The hydrogen peroxide solution is standardised against a known weight of potassium permanganate dissolved in dilute nitric acid. L. DE K.

Estimation of Chromium in Chrome Ore and Ferrochromium. By ERNEST H. SANITER (*J. Soc. Chem. Ind.*, 15, 155—158).—This paper is partly controversial. The author has modified Clark's process (*Trans.*, 1893, 1079) and claims, in opposition to Rideal and Rosenblum (*J. Soc. Chem. Ind.*, 14, 1017), that chrome ore ground only "moderately finely" in an agate mortar can be completely decomposed in 3 minutes. A nickel capsule 2 inches wide and 1 inch deep is used. 0.5 gram of the chrome ore and 3 grams of sodium dioxide are mixed in the capsule, which is then held by tongs in a Bunsen flame. As soon as the mass begins to melt, a circular motion is given to the capsule to prevent the ore from settling. The temperature should be just below a visible red. When cold, the capsule is placed in a large basin and filled with cold water, and after the melt has dissolved it is rinsed with hot water. The solution, diluted to about 300 c.c. with hot water, is then coloured pink by adding potassium permanganate ; 100 c.c. of dilute hydrochloric acid (1 : 1) is now gradually added, and the solution boiled until clear ; 150 c.c. more hot water is added and the boiling continued for 10 minutes, by which time all chlorine is expelled. The cooled solution, now measuring 500 c.c., is titrated with ferrous sulphate and dichromate. At this dilution, the nickel present, derived from the nickel capsule used, does not interfere with the titration.

Ferrochromium is crushed until the whole sample passes through a sieve of 10,000 meshes to the square inch. For 0.3—0.5 gram of substance, 4 grams of sodium dioxide and 0.75 gram of barium peroxide are taken, and the process is the same as before, except that a larger quantity of potassium permanganate is added, to prevent reduction of chromate by the barium peroxide.

[SAMUEL RIDEAL and SIGMUND G. ROSENBLUM], criticising the paper, state that they were unable to get complete decomposition in one fusion unless the chrome ore was very finely ground ; that some sodium dioxide always remained at the end of the fusion and reduced some chromate on acidifying unless previously decomposed by boiling, for which 10 minutes sufficed ; that the addition of barium peroxide is both useless and a source of complications, and that it is better to filter from nickel oxide than to trust to dilution for masking the brown colour it gives with ferricyanide.

M. J. S.

Estimation of Chromium in Ferrochrome and Chromium Steel. By JOS. SPÜLLER and A. BRENNER (*Chem. Zeit.*, 1897, ii, 3—4). —*Assay of Ferrochrome.*—0.35 gram of the finely powdered sample mixed in a hemispherical silver dish with 2 grams of dry powdered sodium hydroxide and covered with 4 grams of sodium dioxide, is heated until the mixture begins to melt, when, as a consequence of the strong chemical action, the whole mass soon becomes liquefied. The dish is then again heated for 10 minutes over a powerful burner, and 5 grams of sodium dioxide is cautiously added, stirring all the while with a silver spatule. After heating for 30 minutes more, another 5 grams of sodium dioxide is added and the heating continued for 20 minutes, when a final 5 grams of the dioxide is added.

When cold, the silver basin is placed in a deep porcelain dish and filled with water; when the lixiviation is completed, which takes a few minutes only, the silver dish is lifted out and well rinsed with hot water. A brisk current of carbonic anhydride is then passed through the liquid for half an hour, the whole allowed to cool, introduced into a litre measure, and made up to the mark with water. After shaking and filtering, 250 c.c. is taken and the chromic acid titrated by Schwarz's method. If the solution of the melt appears green, it is advisable to add first a few c.c. of potassium permanganate solution, and then some more sodium dioxide, when a pure yellow liquid will be obtained.

Assay of Chrome-steel.—Two grams of the sample is dissolved in 20 c.c. of warm hydrochloric acid contained in a porcelain dish, 10 c.c. of dilute sulphuric acid (1:1) is added, and the whole evaporated to dryness; the residue is then transferred to a hemispherical silver dish and heated with 2 grams of sodium hydroxide and 5 grams of sodium dioxide, until the sulphates are decomposed and the mass begins to cake. A strong heat is now applied and another 5 grams of the dioxide is added. When the mass begins to fuse, it is well stirred with a silver spatula, and after 20 minutes another 5 grams of sodium dioxide is added; after another 20 minutes, when the oxidation is complete, a further addition of 5 grams of the soda is made and the mass is allowed to cool. The melt is then extracted as in the former case, but the liquid is made up to 500 c.c. only, and 250 c.c. of the filtrate (1 gram of sample) is taken for the titration of the chromium. In this case, the authors prefer titrating according to Zulkowsky's method; the liquid is put into a long, narrow beaker, mixed with 10 c.c. of a 10 per cent. solution of potassium iodide, and acidified with pure hydrochloric acid. To another beaker containing 20 c.c. of a solution of potassium dichromate (0.9833 gram per litre), 250 c.c. of water is added, then 10 c.c. of a 10 per cent. solution of potassium iodide and a little hydrochloric acid. After being left for 15 minutes in a dark place, both liquids are titrated with solution of sodium thio-sulphate containing 4.96 grams of the salt per litre. The amount of chromium being known in the one solution, the quantity contained in the other is readily calculated.

L. DE K.

Estimation of Nickel in Nickel-steel. By JOS. SPÜLLER (*Chem. Zeit.*, 1897, 21, 243—244).—If the samples contain at least 1 per

cent. of nickel, the amount may be tolerably accurately estimated by dissolving 2 grams in 60 c.c. of nitric acid of sp. gr. 1.2, boiling until the nitrous fumes are expelled, and precipitating the iron by adding an emulsion of zinc oxide; the green filtrate is then collected in a suitable colorimeter, which may be improvised by using a beaker of about 7 cm. diameter placed on white glazed paper.

In a similar beaker is placed the filtrate obtained by dissolving 2 grams of a standard sample of nickel steel, removing the iron as before; on comparing the tints, the amount of nickel in the commercial sample can readily be estimated. L. DE K.

Separations with Alkali Acetates. II. Nickel from Iron. III. Cobalt and Manganese from Iron. By HARRY BREARLEY (*Chem. News*, 1897, 76, 49—51, 165—167. Compare Abstr., 1896, ii, 676).—*Nickel from Iron.*—The substance is dissolved in hydrochloric acid and oxidised with nitric acid, or, if only a small quantity, or no carbon is present, it is dissolved in nitric acid directly, diluted, cooled, an alkali carbonate added until a slight permanent precipitate is formed, and then 10 c.c. of acetic acid. The liquid is diluted to about a litre with hot or cold water, 10 to 12 c.c. of ammonium (sodium) acetate solution added for each gram of iron in solution, adding more if no turbidity appears on heating to near the boiling point. If turbidity appears too soon, the heating is stopped when the precipitate becomes flocculent and the solution nearly colourless, and if the precipitation is slow after the turbidity has appeared at the boiling point, the heating is prolonged. An aliquot part of the liquid is filtered through asbestos, cooled, neutralised, a measured quantity of dilute ammonia added, and the liquid then titrated with potassium cyanide and silver iodide. For a rapid result, or when there is sufficient ferric hydroxide to interfere, excess of cyanide is run in, the liquid filtered through asbestos, and titrated back with silver nitrate. By using ammonia salts, as much as 0.8 gram of nickel to 1 gram of iron may be estimated; the usual small amounts of manganese or chromium do not matter, but copper and larger amounts of manganese, chromium and aluminium must be removed. Large quantities of ammonia cause error, but the acetate, chloride, and nitrate do not do so appreciably. The last two, however, lessen the amount of alkali required to neutralise the iron solution and lower the temperature at which turbidity appears and also deepen it; whereas the sulphate, chloride, and nitrate lessen the turbidity in the order given. Artificial alizarin can be used as an indicator when neutralising the free acid; it gives a purple coloration in the presence of silver iodide, which changes to pink when the latter is dissolved.

Cobalt and iron can be separated as in the preceding case of nickel; its presence in the solution causes a variable and transitory darkening on the addition of cyanide, and, moreover, the silver iodide dissolves before all the cobalt is saturated. Therefore, the titration has to be modified, and the cyanide, which is standardised with cobalt in this case, is run in in excess and after a while titrated back with silver nitrate.

In manganese separations, and, in fact, in all these separations, the acetates should be used as sparingly as possible. D. A. L.

Analysis of Alloys of Tin, Antimony, and Copper. By GUSTAVE W. THOMPSON (*J. Soc. Chem. Ind.*, 15, 179—182).—Commercial alloys of the above metals frequently contain, in addition, phosphorus, arsenic, bismuth, cadmium, nickel, and cobalt. The course of the analysis will naturally be modified by the absence of one or more of the metals, but the following method applies to cases where all are present. The alloy (1 gram) is dissolved in 100 c.c. of a solution made up as follows:—20 grams of potassium chloride in 500 c.c. of water, 400 c.c. of concentrated hydrochloric acid, 100 c.c. of nitric acid of 1·4 sp. gr. After concentrating to 50 c.c., the solution is cooled, precipitation of the lead chloride is completed by adding 2 vols. of 95 per cent. alcohol, and the precipitate, after being washed with a mixture of alcohol and hydrochloric acid (4:1), is dissolved in ammonium acetate, precipitated as chromate, and weighed. The filtrate from the lead chloride is evaporated to dryness, heated for 20 minutes with 10 c.c. of potassium hydroxide (1:5) and 20 c.c. of 3 per cent. hydrogen peroxide (the object of which is to prevent separation of sulphur with the antimony sulphide), then mixed with 10 grams of ammonium oxalate, 10 grams of oxalic acid, and 200 c.c. of water, and treated with hydrogen sulphide for 45 minutes at a nearly boiling temperature; this precipitates copper and antimony (also bismuth, cadmium, and partially nickel and cobalt), but leaves the tin in solution. After expelling hydrogen sulphide from the filtrate, the tin (with traces of nickel and cobalt, and also of iron, if present) is precipitated by electrolysis the solution for 12 hours with a current of 0·5 ampère. The copper and antimony sulphides are separated by heating with potassium hydroxide, the copper is converted into nitrate and titrated with potassium cyanide in ammoniacal solution (or precipitated electrolytically if in large amount), whilst the antimony, after being converted into antimonic chloride by boiling with hydrochloric acid and potassium chlorate, the excess of chlorine being expelled and the sulphur filtered off, is reduced to trichloride by adding potassium iodide, and estimated from a titration of the iodine liberated. Arsenic accompanies the antimony, and is best estimated in a separate portion by distilling the hydrochloric acid solution with sodium thiosulphate. Bismuth, cadmium, nickel, and cobalt sulphides would remain with the copper sulphide after separation of the antimony. Phosphorus is best estimated by Dudley's method. For the minutest details of the operations, and for simple methods suited only to special alloys, the original should be consulted. M. J. S.

Estimation of Organic Matter by Chromic Acid. By JOSEPH BARNES (*J. Soc. Chem. Ind.*, 15, 82—84).—With the view of superseding the old permanganate method of ascertaining the amount of oxygen absorbable by the organic matter in a water by a process in which the oxidation should be more energetic, the author has employed a hot mixture of chromic and sulphuric acids. The solutions used are: one containing 6·2 grams of potassium dichromate and 50 c.c. of concentrated sulphuric acid per litre, a solution of ferrous sulphate containing about 36 grams of the crystallised salt with 200 c.c. of sulphuric acid per litre, and a permanganate solution. To make an

estimation, 50 c.c. of the water is mixed with 25 c.c. of concentrated sulphuric acid and 10 c.c. of the chromate solution, and is heated on the water bath for 1 hour. It is then rapidly cooled, 10 c.c. of the ferrous solution and 500 c.c. of cold water are added, and the excess of ferrous iron is titrated with the permanganate.

Another method is described in which permanganic acid is used: 100 c.c. of the water is mixed in a stoppered bottle with 10 c.c. of dilute sulphuric acid (1:2) and 10 c.c. of permanganate solution (4 grams per litre); and the bottle is kept at 21° for two and a half hours. An excess (10 c.c.) of ferrous sulphate is then added, and the excess titrated by a weaker permanganate solution (1 c.c. = 0.0005 gram of oxygen).

Blank experiments are required in both methods. A table is given showing the amount of oxygen absorbed by various organic matters in each process. The results are purely empirical, and are influenced (but in opposite directions) by variations in the amount of organic matter taken.

M. J. S.

Fehling's Solution. By MILORAD R. JOVITSCHITSCH (*Ber.*, 1897, 30, 2431—2432).—Mineral acids, such as sulphuric, nitric, and hydrochloric acids, reduce Fehling's solution, especially if the reaction be carried out in only slightly alkaline solution, the reduction being probably due to the decomposition of the tartaric acid by the mineral acid present; it is this, probably, which renders it necessary to carry out the tests with Fehling's solution in a strongly alkaline solution.

J. F. T.

Gravimetric Estimation of Sugars by Fehling-Allihn's Process. By GOTTWALT AMBÜHL (*Chem. Zeit.*, 1897, 21, 137—138).—The author has analysed 38 samples of wine, 4 of honey, and 4 of urine by the above process, and has tabulated the results.

The table shows that there is no necessity to reduce the cuprous oxide to metallic copper, as a direct weighing of the former gives sufficiently accurate results.

L. DE K.

Estimation of Furfuraldehyde by Means of Phloroglucinol. By CONSTANTIN COUNCLER (*Chem. Zeit.*, 1897, 21, 2—3).—The author (*Abstr.*, 1895, ii, 144) states that it is of great importance to use phloroglucinol free from diresorcinol. Unless the amount of furfuraldehyde is very small, it is advisable to take an aliquot part only of the distillate for precipitation.

The amount of furfuraldehyde yielded on distilling a sample of brown coal with hydrochloric acid was no less than 0.22 per cent., corresponding with 0.408 per cent. of pentosan calculated on the dried sample.

L. DE K.

Colour Reactions of Pyruvic Acid. By LOUIS SIMON (*Compt. rend.*, 1897, 125, 534—536).—See this vol., i, 64.

Estimation of Fat in Animal Substances. By ELLY BOGDANOW (*Pflüger's Archiv.*, 1897, 68, 431—433).—See this vol., ii, 84.

The Iodine Number of Fats and Oils. By HUGO SCHWEITZER and EMIL E. LUNGWITZ (*J. Soc. Chem. Ind.*, 14, 1030—1035).—The authors have already proved (*Abstr.*, 1896, ii, 398) that in Hübl's

process, substitution, as well as addition, of iodine occurs. They now show that the use of methylic alcohol, recommended by Fahrion, whilst it does not affect the total amount of iodine absorbed, increases the proportion employed in substitution. When the mercuric chloride is omitted, the iodine absorption consists chiefly, or, in the case of methylic alcohol, entirely, of substitution, but the proportion of substitutive iodine is not diminished by using more mercuric chloride than in Hübl's standard reagent. In chloroform and ethylic ether solutions, substitution also occurs to a large extent; but in carbon bisulphide and carbon tetrachloride solutions the absorption is additive only. Mercuric bromide, whether in ethylic or methylic alcohol, gives more substitution than mercuric chloride. Various other metallic chlorides were tried, employing ethylic alcohol solutions. With manganous chloride (or bromide), cobalt chloride, and nickel chloride, very little substitution occurred, but the total absorption was low and variable.

By working with carbon bisulphide solutions, in the presence of mercuric chloride, and at an elevated temperature ($50-79^{\circ}$) in stoppered bottles and therefore under pressure, the iodine absorption may be made to exceed that produced by Hübl's normal process, being at the same time a purely additive one. In the case of oleic acid, the absorption exceeds that theoretically required, and this raises doubts as to the constitution of oleic acid.

M. J. S.

Recognition of Margarine by means of Dimethylamidoazobenzene. By ALFRED PARTHEIL (*Chem. Zeit.*, 1897, 21, 255—256).—In order to detect the presence of small quantities of margarine in butter, it has been proposed by Soxhlet to order all margarines to be mixed with a small quantity (1:100,000) of phenolphthalein. Any one would then be able to recognise adulterated butter by the reddish colour when the sample is mixed with a little soda. The use of phenolphthalein is, however, objectionable for many reasons, and the author now proposes to use dimethylamidoazobenzene dissolved in oil instead. This turns red on adding dilute sulphuric acid. L. DE K.

Analysis of Fats: Estimation of Unsaponifiable Matter. By JULIUS LEWKOWITSCH (*J. Soc. Chem. Ind.*, 15, 13—14).—The processes in use may be classed under two heads: extraction of the soap solution with ether or light petroleum, and extraction of the dry soap by solvents. With certain oils, such as shark-liver oil, and some kinds of whale oil, both methods are unsuitable when petroleum is used, since the unsaponifiable matter is sparingly soluble in the cold petroleum, and at the same time much soap dissolves. The latter may be removed by washing the petroleum solution with 50 per cent. alcohol, but it is safer to use ethylic ether as the solvent, and correct for any dissolved soap by incinerating the residue left on evaporation and estimating the alkalinity of the ash.

M. J. S.

Analysis of Fats: Wool Wax. By JULIUS LEWKOWITSCH (*J. Soc. Chem. Ind.*, 15, 14—15).—Wool fat (Yorkshire grease) contains a considerable proportion of free fatty acids and true waxes, with a small quantity of free alcohols. The neutral portion, for which the author proposes the name "wool wax," is now obtainable in

commerce. A specimen yielded 51·8 per cent. of unsaponifiable matter soluble in ether, also easily soluble soaps, and sparingly soluble soaps. The unsaponifiable matter had a melting point of 46—48°, iodine number 26·35. From its gain in weight when boiled with acetic anhydride (8·26 per cent.), cetylic alcohol must be almost absent, and the iodine number shows that there cannot be much cholesterol present. When heated at 250° with soda-lime, 80 per cent. of the alcohols was recovered unchanged, only 6 per cent. of fatty acids, of melting point 51—53°, being recoverable from the soap formed. The easily soluble soaps from the original substance yielded 25·5 per cent. of fatty acids, in which the presence of lactones was demonstrated. The sparingly soluble soaps also yielded fatty acids and lactones amounting to 26 per cent. The iodine values, &c., of these fractions are given, but no conclusions are drawn from the admittedly incomplete experiments. M. J. S.

Estimation of Resin in Fats and Soaps.—By JOHN LANDIN (*Chem. Zeit.*, 1897, 21, 25). The author has not succeeded in getting accurate results by using Gladding's silver process or Cornette's brine method.

The following modification of the Twitchell-Wilson process is recommended:—Three grams of the isolated fatty acids is dissolved in 30 c.c. of absolute alcohol contained in a flask surrounded by cold water, and dry hydrogen chloride is then passed through the solution for 45 minutes; this converts the fatty acids into the corresponding ethylic salts, whilst the resinous acids remain unaltered. The mixture, in a separating funnel, is now treated with 125 c.c. of hot water, and shaken with 75 c.c. of light petroleum to dissolve the resin. The aqueous layer is then drawn off, and the petroleum solution shaken with a mixture of 0·5 gram of potassium hydroxide, 5 c.c. of alcohol, and 50 c.c. of water, to remove the resin; from the alkaline solution, the resin acids are liberated by acidifying with hydrochloric acid, collected on a tared filter, dried, and weighed. L. DE K.

Estimation of Caffeine in Tea. By EUSTACE H. GANE (*J. Soc. Chem. Ind.*, 15, 95—96). The process suggested by Allen was found to give either identical or higher yields, a purer product, and greater facility of execution than the method of Paul and Cownley, which is usually employed (*Abstr.*, 1888, 539). The following slight modification is preferred. Six grams of the finely powdered tea is boiled with 600 c.c. of water for 6 or 8 hours in a reflux apparatus; 4 grams of lead acetate is then added, the boiling continued for 10 minutes longer, and the decoction filtered. 500 c.c. of the filtrate is evaporated to 50 c.c., and the excess of lead is removed by sodium phosphate. Finally, the liquid is concentrated to about 40 c.c., and the caffeine extracted by shaking five times with chloroform. M. J. S.

Opium Assay. By DAVID B. DOTT (*J. Soc. Chem. Ind.*, 15, 91—94).—The British Pharmacopœia process for the estimation of morphine is vitiated by several erroneous features, especially the subdivision of the solution, the great dilution, the large amount of alcohol, and the drying at 100°. Squibb's process, official in the United

States, is more satisfactory, but is not free from objections. The author proposes two processes: (A.) Exhaust 10 grams of opium with alcohol of 0.92 sp. gr., evaporate to one-fourth, dilute this with half its volume of water containing 0.05 gram of ammonium oxalate, the object of which is to decompose the calcium meconate. Add ammonia until the liquid remains just perceptibly acid. After an hour, filter, concentrate to 8 c.c., transfer to a 100 c.c. flask by means of 2 c.c. of water, and 3 c.c. of alcohol, add 2.5 c.c. of ammonia (0.96 sq. gr.), and 25 c.c. of ether. Cork the flask, and shake occasionally during an hour. After 18 hours, decant the ether, collect the precipitate on a tared filter, wash with morphinated water, dry, wash with chloroform, and dry at 60°, at which temperature the precipitate has the formula $8C_{17}H_{19}NO_3 + 9H_2O$. It is very free from impurities.

For method B, which is more expeditious, but gives a less pure precipitate, see Abstr., 1896, ii, 283. M. J. S.

Estimation of Alkaloids. By E. H. FARR and ROBERT WRIGHT (*Pharm. J. Trans.*, 1897, 58, 202—203).—The estimation of morphine in opium by the official process of the British Pharmacopœia gives good results when carried out as follows. The very finely powdered opium (14 grams) is rubbed into a uniform paste with freshly slaked lime (6 grams) and water (40 c.c.), then 100 c.c. more water is added and the mixture stirred occasionally for half an hour; 104 c.c. of the filtered mixture, which is supposed to represent 10 grams of opium, is shaken for half an hour with ammonium chloride (4 grams), ether (50 c.c.), and rectified spirit (11 c.c.), and then allowed to remain for 12 hours. It is essential that the proportion of alcohol should not be too high, as otherwise more morphine is retained in the mother liquor. The ethereal layer is then removed and the mixture again extracted with 20 c.c. of ether, to ensure the removal of all substances soluble in that liquid; finally, the crystals of morphine are collected on tared filters, washed with a little distilled water, dried first by pressing between filter paper, then at a gentle heat, and finally at 96—100°, until a constant weight is obtained. The opium must be in a very fine powder, as otherwise a loss of morphine occurs amounting sometimes to 5 per cent. It is also advantageous to finish the drying of the morphine at 110°; some samples which were examined by the authors after drying at 100°, lost from 1.6 to 6.61 per cent., when heated at 110°. The loss of morphine in the mother liquors amounts to 0.1 gram for every 100 c.c. of the filtrate.

For the estimation of morphine in tincture of opium, the details are as follows: 80 c.c. of the tincture is evaporated to 20 c.c. at a low temperature, treated with freshly slaked lime (3 grams), and made up to 85 c.c.; 50 c.c. is then filtered into a 4 oz. bottle fitted with an accurately-ground stopper, and mixed with ammonium chloride (2 grams), ether (30 c.c.), and alcohol (5 c.c.). After the mixture has been shaken for half an hour and allowed to remain 12 hours, the layer of ether is removed by means of a pipette and the mixture shaken with 15 c.c. more ether, this being removed by means of a pipette, and filtered through tared filter papers. The filter is washed with a little ether, the residual ether allowed to evaporate, and then the

crystals of morphine are washed on to the filter, and washed with morphinated water until the washings are colourless. The crystals, after drying at a gentle heat, are heated at 110° for one hour and weighed. 0.3 gram of the crystals is dissolved in a slight excess of N/10 sulphuric acid, and the excess of acid estimated by N/10 soda solution, using litmus paper as indicator. To the amount of anhydrous morphine in the total weight of the crystals as indicated by the titration, 0.05 gram is to be added. The combined weight multiplied by 2 will be the percentage of morphine in the tincture. The results agree well with those obtained by Dott's and by Teschemacher and Smith's processes.

The official process for the estimation of water in alkaloids consists in drying them by the heat of boiling water; in the case of morphine, as shown above, this temperature is not sufficient. In the case of the cinchona alkaloids and the salts of quinine, however, perfect desiccation may be obtained if sufficient time is given, but much time is saved by drying at 120° . Alkaloidal residues and extractive matters should always be dried in a flat-bottomed dish, so as to allow them to spread out in a thin layer.

The authors corroborate the statement of Cownley that *Quininæ sulphas* (official sulphate of quinine) gradually loses water of crystallisation on exposure to the air, until but 2 molecules are retained; also the anhydrous salt rapidly absorbs water, 1 gram on exposure to the air absorbed 0.015 gram of water in 7 minutes. They suggest that the sulphate with $2\text{H}_2\text{O}$ should replace the one now official in the British Pharmacopœia. *Quininæ hydrochloras*, when dried, is more hygroscopic than the sulphate, 0.626 gram, on exposure to the air, absorbed 0.017 gram of water in 6 minutes, and in 3 hours was converted into the salt with $2\text{H}_2\text{O}$.

E. C. R.

New Methods of Testing Indigo. By B. WILLIAM GERLAND (*J. Soc. Chem. Ind.*, 15, 15—17).—The process most in use, depending on reduction and the weighing of the recovered indigotin, is untrustworthy, since part of the indigotin is lost, and that which is recovered is very impure. The author makes use of the solubility of indigotin in hot nitrobenzene, and its almost complete separation on cooling (see Abstr., 1890, 311). The following simple extraction apparatus is employed. A test-tube 200 mm. long and 40 mm. diameter is clamped above a lamp. Centrally within it, the filter, consisting of a thin glass tube 45 mm. long and 20 mm. diameter, over the lower end of which calico, on which is placed a little paper pulp, is wired, is hung from a tube 8 mm. in diameter and 500 mm. long, which serves as a reflux condenser, and passes through a funnel resting on the mouth of the test-tube. It is connected with an aspirator, the action of which prevents escape of nitrobenzene vapour, and also the recondensation of any steam. Twenty-five c.c. of nitrobenzene, saturated in the cold with indigotin, is placed in the test-tube, and, by careful regulation of the flame and aspirator, the extraction of 0.5 gram of indigo is complete in $\frac{1}{2}$ —1 hour. The crystallised indigotin is collected on an extracted, weighed filter, washed with benzene, and dried. It still contains 3—6 per cent. of impurities, from which it can be freed by

prolonged treatment with hydrochloric acid and hydrogen peroxide, being thereby rendered fit for weighing or for titration by Bernthsen's hyposulphite process. Owing to the solubility of indirubin in cold nitrobenzene, the total colouring matter is underestimated to the extent of about 0.1—0.2 per cent.

By heating indigo with sulphuric acid of 1.67 sp. gr. (40 c.c. to 0.5 gram) in a water bath for an hour, the idigotin is wholly converted into the monosulphonic acid, which dissolves, and can be separated from the residue by filtering through a sand filter with suction, and washing with acid of the same strength heated to 100°. On diluting the solution with 2 or 3 volumes of water, the monosulphonic acid is completely precipitated. It is best to collect it on a sand filter, and wash with water containing 20 per cent. of SO_3 . It is then dried and digested at 100° with concentrated sulphuric acid, whereby it is converted into the disulphonic acid, which can be readily removed from the filter by water. It still, however, contains coloured impurities which vitiate the titration with hyposulphite. But if the raw indigo has been digested for some time in the cold with hydrochloric acid and hydrogen peroxide, then boiled, washed with boiling water and dried before treatment with sulphuric acid, the sulphindigotic acid is sufficiently pure to give good results on titration. The titration apparatus resembles that used by Tiemann and Preuss (*Abstr.*, 1880, 138). The indirubin is estimated as indigotin, and the results are 0.3—0.4 per cent. higher than those obtained by the nitrobenzene process. M. J. S.

Estimation of Free Humic Acid in Peaty Soils. By BRUNO TACKE (*Chem. Zeit.*, 1897, 21, 174—175).—The direct estimation of humic acid is impracticable on account of the colouring matters contained in the soils, but the author has devised an indirect process based on the decomposition of calcium carbonate by humic acid.

The apparatus consists of a generating flask furnished with a trebly perforated cork, through which pass three tubes; one of these is connected with a constant hydrogen apparatus, the second is fitted to an indiarubber tube with a screw-clamp, whilst the third is connected with a Pettenkofer's absorption tube.

The sample is put into the generating flask with 100 c.c. of boiled water, and a current of purified hydrogen is passed through the liquid for an hour to expel all the air; the absorption tube is then filled with 100 c.c. of N/10 soda, and an emulsion of calcium carbonate is introduced through the indiarubber tube. The current of hydrogen is kept up for 3 hours, when the contents of the absorption tube are titrated with N/10 hydrochloric acid, after adding barium chloride to precipitate the carbonate. The diminution in alkalinity represents the amount of carbonic anhydride given off by the calcium carbonate.

Although more carbonic anhydride is given off when the mixture is heated, the author thinks that the amount evolved in the cold is the true measure of the humic acid in the soil. L. DE K.

Modification of Stutzer's Process for Estimating Proteids in Substances Rich in Starch. By HEINRICH C. TRYLLER (*Chem. Zeit.*, 1897, 21, 54).—The sample is treated according to Stutzer's

directions, but after adding the alum and the emulsion of copper hydroxide, it is allowed to cool to 65°, and 10 c.c. of a 20 per cent. malt-infusion is added. This rapidly liquefies the starch and facilitates the filtration.

The residue on the filter is then tested for nitrogen by Kjeldahl's process, allowance being made for any nitrogen contained in the malt solution and the filter paper.

L. DE K.

General and Physical Chemistry.

New Lines in the Spectra of Oxygen and Thallium. By HENRY WILDE (*Compt. rend.*, 1897, 125, 708—709).—When a powerful electric spark condensed by means of a small Leyden jar is passed from thallium electrodes through air under a pressure of 20 atmos., three red lines are seen which are not visible when a similar spark is passed through nitrogen from platinum electrodes. Two of the lines, 7760 and 7160, are due to oxygen, and the third, 6955, to thallium. The oxygen line, 7160, is useful for detecting the presence of oxygen when separating argon from air by the sparking method. The conclusion of Stas, that the high temperature spectrum of thallium consists of a single line only, was due to the fact that he did not use a sufficiently powerful arc. The spectrum of thallium is the same whether observed in nitrogen or in air and therefore the lines and bands cannot be attributed, as Stas supposed, to thallium oxide. C. H. B.

Fluorescence and Chemical Constitution. By RICHARD E. MEYER (*Zeit. physikal. Chem.*, 1897, 24, 468—508).—The fluorescence of organic compounds may be regarded as due to the presence of certain atomic groups which remain unchanged in the various fluorescent derivatives; these the author terms fluorophores or fluorphoric groups. In order, however, that the fluorescence may be developed, it is further necessary that the fluorophore be situated between two heavy atomic groups, usually benzene nuclei. In the derivatives of fluoran (Abstr., 1892, 970) embracing the fluoresceins, naphthofluorans, rhodamines, &c., the fluorophore is the pyrone group, which, although not fluorescent itself, becomes so in the diphenyl derivatives. The xanthenes contain the same fluorophore, and the xanthenes, its reduction product, and in all these groups of compounds the effect of substitution is very marked. In general, the entrance of heavy atoms or groups into the benzene nuclei diminishes the fluorescence, the effect being largely dependent on both nature and position of the substituent; thus the presence of hydroxyl groups in a position other than that of the fluorescein hydroxyls destroys or greatly weakens the fluorescence of the fluoran and xanthone compounds. In the anthracene group, only its direct derivatives, and not those of anthraquinone, are fluorescent. The acridine compounds contain the fluorophore $\text{CH} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \end{array} \text{N}$ and the effect of the position of the substituent is here also very marked, benzoflavine which contains both amido-groups in the "fluorescein position" being far more strongly fluorescent than the isomeric chrys-aniline. The substitution of sulphur for oxygen in the pyrone ring does not destroy its fluorphoric character, as the thiopyrone derivatives also exhibit weak fluorescence. The azine, oxazine, and thiazine rings also act as fluorophores in the phenazines, phenazoxines and thiodiphenylamine compounds, which include many important fluorescent dyes as mauveine, the safranines and allied naphthalene compounds,

the indulines, Lauth's violet, and methylene-blue, which exhibits, although previously unrecorded, a reddish-violet fluorescence. The solvent has also a direct influence, as some compounds fluoresce strongly in some solutions, but not at all in others, and this difference is not always capable of being explained by dissociation changes.

L. M. J.

Conductivity of Electrolytes for very rapid Electrical Vibrations. By J. A. ERSKINE (*Ann. Phys. Chem.*, 1897, [ii], 62, 454—459).—For vibrations of the period 1.3×10^8 , the conductivity of the electrolytes examined agrees closely with that determined by Kohlrausch with the constant current.

H. C.

Electrolytic Conductivity of Trichloroacetic Acid. By PAUL RIVALS (*Compt. rend.*, 1897, 125, 574—576).—The author has determined, by Bouty's method, the electrolytic conductivity of solutions of trichloroacetic acid at 16° for degrees of dilution comprised between $v = 1$ litre and $v = 128$ litres, with the following results.

Values of v .	Values of $\mu \cdot 10^{-7}$.	Values of v .	Values of $\mu \cdot 10^{-7}$.	Values of v .	Values of $\mu \cdot 10^{-7}$.
1 litre	178.3	4 litres	260.6	16 litres	289.5
2 litres	226.4	6 litres	268.5	32 litres	304.3
3 litres	247.5	8 litres	279.0	128 litres	317.0

μ can be represented as a function of v , either by a parabolic formula, or more simply as a linear function of $1/\sqrt{v}$.

$$\mu = 331.7 \times 10^{-7} (1 - 0.463/\sqrt{v}).$$

If μ_{∞} , the limit of conductivity, has the value $\mu_{\infty} = 331.7 \times 10^{-7}$ and $m = \mu/\mu_{\infty}$, then m represents the proportion of acid dissociated and $m = 1 - 0.463/\sqrt{v}$.

Consideration of these results, together with the author's earlier determinations of the heat of dilution of trichloroacetic acid at various concentrations, shows that the heat of dissolution and the degree of dissociation are both linear functions of $1/\sqrt{v}$, or, in other words, the heat of dilution is proportional to the fraction of acid dissociated. The molecular heat of electrolytic dissociation of trichloroacetic acid is +4.17 Cal., and the heat of neutralisation by potassium hydroxide calculated on this basis by means of Ostwald's formula agrees closely with the experimental value.

C. H. B.

Resistance and Specific Heat of some Oxides and Sulphides of Iron. By ANTAL ABT (*Ann. Phys. Chem.*, 1897, [ii], 62, 474—481).—Prisms were cut of the following minerals, of the length in centimetres and cross-section in square millimetres given below, and the resistance r in ohms of each prism directly measured, and from this the resistance w for a prism of 1 centimetre length and 1 square centimetre area calculated in each case. The results are given in the table on following page.

The great difference in the magnetites is mainly due to the silica which they contain, as the resistance of quartz is very high.

Mineral.	Locality.	Length.	Area.	r .	w
Nickel ore N_1 ...	Dobsina	4·961	28·136	0·069	0·0032
" " N_2 ...	"	9·970	172·922	0·043	0·0074
Pyrrhotite P_1	Alsó Jára	10·310	196·000	0·044	0·0084
" " P_2	"	10·030	196·000	0·052	0·0102
Chalcopyrite	Oláhlápos	14·600	196·000	0·758	1·0176
Pyrites	Felsőbánya	0·375	317·809	1·085	9·2000
Magnetite M_1	Moravitzá	14·596	196·000	52·560	7·0600
" M_2	"	14·610	196·000	80·250	10·7600
" M_3	"	0·086	295·333	2·860	97·8900
" M_4	"	0·083	259·339	12·451	387·6400
" M_5	"	0·082	257·732	45·608	1433·5100
" M_6	"	9·948	193·000	8550·000	1684·5500
" M_7	"	4·981	23·619	36500·000	1714·7100
" M_8	"	16·630	201·640	36500 +	4400 +
" M_9	"	14·590	196·000	36500 +	4900 +
Hæmatite H_1	"	4·987	24·682	29000·000	1430·5200
" H_2	Kakukhegy (Hargitta)	0·115	54·780	1309·182	6214·6400
" H_3	Moravitzá	14·475	177·956	36500 +	6500 +
Siderite	Dobsina	10·000	196·000	36500·000	7154·0000

The specific heats, c , of the following minerals were determined, their composition being at the same time ascertained by analysis.

Mineral.	SiO_2	Fe	S	O	c
Pyrrhotite	4·42	57·68	37·66	—	0·1539
Magnetite	5·72	68·10	—	25·93	0·1655
Hæmatite	2·13	67·15	—	28·78	0·1745
Nickel ore from Dobsina	—	—	—	—	0·1040

H. C.

Theory of Solutions. By BRONISLAW PAWLEWSKI (*Ber.*, 1897, 30, 2805—2807).—The melting points of mixtures of paradibromobenzene and metachloronitrobenzene follow the normal course, the eutectic point $35\cdot7^\circ$ occurring with the mixture containing 32·99 per cent. paradibromobenzene, and 67·01 per cent. metachloronitrobenzene. Mixtures of paradibromobenzene and parachloronitrobenzene, on the other hand, are abnormal in their behaviour, as three distinct minima occur on the melting point curve. No explanation of this behaviour can be given.

H. C.

Influence of Molecular Association on the Reduction of the Freezing Point and the Osmotic Pressure of Solutions. By HOLLAND CROMPTON (*Ber.*, 1897, 30, 2720—2725).—By combining the relation $rd/T = 0\cdot099x/a$ (*Trans.*, 1897, 925) with the van't Hoff equation for the reduction of the freezing point $E = 0\cdot02T^2/r$, for monomolecular compounds $E/Td = 0\cdot2$, and for associated compounds $E/Td = 0\cdot2a/x$. Tables are given of the values of E/Td which show a

fair agreement with theory in the case of the monomolecular compounds, but discrepancies are observed among the associated compounds. To account for the latter, the view is advanced that van't Hoff's equation should be modified when the solvent used is associated, and that for associated as well as for monomolecular solvents, $E/Td = 0.2$.

H. C.

Densities of Easily Liquefiable Gases. By ANATOLE LEDUC (*Compt. rend.*, 1897, 125, 571—573).—The following results were obtained.

Carbonic anhydride..	1.5287	Chlorine.....	2.491
Nitrous oxide.....	1.5301	Ammonia	0.5971
Hydrogen sulphide...	1.1895		

The author's previous determinations have given 1.2692 for hydrogen chloride and 2.2639 for sulphurous anhydride. All these determinations the author regards as less exact than those that he has made with gases difficult to liquefy. For example, the condensation of the gas on the walls of the glass vessel introduces an error the magnitude of which cannot be calculated.

C. H. B.

Dissociation of Saline Hydrates and Analogous Compounds. By HENRI LESCŒUR (*Ann. Chim. Phys.*, 1896, [vii], 19, 213—234, 416—432 and 537—550. Compare Abstr., 1889, 815; 1893, ii, 364; 1894, ii, 343, and 1895, ii, 269).—The following have been examined: Lithium, cadmium, manganese, cobalt, nickel, ferrous and uranium sulphates; strontium, magnesium, zinc, cadmium, manganese, cobalt, nickel, copper, bismuth, and uranium nitrates; potassium carbonate, potassium hydrogen carbonate, borax, normal potassium oxalate, potassium ferrocyanide, and sodium thiosulphate.

The author points out the necessity of crystallising the sulphates from a perfectly neutral medium, as minute quantities of free sulphuric acid change the nature of the hydrates formed. The same applies to the nitrates.

	Hydrate formed from neutral solution.	Compound precipitated by addition of sulphuric acid.
Sodium sulphate.....	$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$	Slight turbidity only.
Potassium „	K_2SO_4	KHSO_4 .
Ammonium „	$(\text{NH}_4)_2\text{SO}_4$	NH_4HSO_4 .
Magnesium „	$\text{MgSO}_4 + 7\text{H}_2\text{O}$	Slight turbidity.
Zinc „	$\text{ZnSO}_4 + 7\text{H}_2\text{O}$	$\text{ZnSO}_4 + \text{H}_2\text{O}$.
Cadmium „	$\text{CdSO}_4 + 4\text{H}_2\text{O}$	$\text{CdSO}_4 + \text{H}_2\text{O}$.
Manganese „	$\text{MnSO}_4 + 5\text{H}_2\text{O}$	$\text{MnSO}_4 + \text{H}_2\text{O}$.
Ferrous „	$\text{FeSO}_4 + 7\text{H}_2\text{O}$	$\text{FeSO}_4 + \text{H}_2\text{O}$.
Nickel „	$\text{NiSO}_4 + 6\text{H}_2\text{O}$	$\text{NiSO}_4 + \text{H}_2\text{O}$.
Cobalt „	$\text{CoSO}_4 + 7\text{H}_2\text{O}$	$\text{CoSO}_4 + \text{H}_2\text{O}$.
Uranium „	$\text{UO}_2\text{SO}_4 + 3\text{H}_2\text{O}$	$\text{UO}_2\text{SO}_4 + \text{H}_2\text{O}$.

The sulphates, with the exception of sodium sulphate, resemble one another in the fact that they yield hydrates $\text{MSO}_4 + \text{H}_2\text{O}$. This hydrate, as a rule, is only dissociated at a fairly high temperature.

The hydrate $\text{CaSO}_4 + \frac{1}{2}\text{H}_2\text{O}$ begins to dissociate at about 100° , and the hydrate, $\text{CuSO}_4 + 3\text{H}_2\text{O}$, at 100° , has a tension of 525 mm.

The maximum tensions at 20° of saturated solutions are

Zinc sulphate	about 15.3 mm.	Cobalt sulphate	about 13.7 mm.
Copper „	„ 15.2 „	Cadmium „	„ 12.9 „
Ammonium sulphate „	„ 14.8 „	Lithium „	„ 12.4 „
Magnesium „	„ 14.5 „	Sodium „	„ 12.0 „
Potassium „	„ 14.4 „	Manganese „	„ 11.8 „
Nickel „	„ 14.4 „	Uranium „	„ 10.8 „

The most common hydrate met with among the nitrates is that with 6H₂O. A second type is with 3H₂O which is generally formed by the dehydration of the first type. The maximum tensions, at 20°, of saturated solutions are

Potassium nitrate	about 15.0 mm.	Zinc nitrate	about 9.6 mm.
Barium „	„ 14.8 „	Cobalt „	„ 9.3 „
Strontium „	„ 14.6 „	Calcium „ (4H ₂ O)	„ 9.3 „
Sodium „	„ 11.15 „	Nickel „	„ 8.5 „
Ammonium „	„ 9.1 „	Copper „	„ 7.9 „
Uranium „	„ 12.2 „	Manganese nitrate „	„ 7.4 „
Cadmium „	„ 10.0 „		J. J. S.

Osmotic Pressure and Electrolytic Dissociation. By ISIDOR TRAUBE (*Ann. Phys. Chem.*, 1897, [ii], 62, 490—506).—If in one litre of the co-volume of any liquid there are present N gram-molecules, as the author has shown in previous papers, the pressure will be $22.38N$ atm. If we imagine water and a sugar solution separated by a semi-permeable membrane, the water containing N molecules per litre co-volume and the sugar solution N molecules of water to ν molecules of sugar, the ν molecules may, according to the author's view, be considered to enter into unstable union with a molecules of water, thus producing the observed contraction in volume, and the number of water particles which will enter the membrane from the two opposite sides will be $N : (N - a\nu)$. Hence on the side of the solution the pressure will be less than that on the side of the water by $22.38 a\nu$ atm. If $a = 1$ the observed pressure accords with the van't Hoff theory, and, therefore, the diminution in pressure on the side of the solution, due to the union of the dissolved substance and the water, is the osmotic pressure. Poynting (*Phil. Mag.*, 1896, [v], 42, 289) has already shown that, assigning this origin to the osmotic pressure, the majority of the observed relations are at once accounted for. The exceptions observed in the case of electrolytes are explained by variations in the value of a , and it is unnecessary to assume electrolytic dissociation in these instances. H. C.

Causes of Osmotic Pressure and of the Simplicity of the Laws of Dilute Solutions. By WILLIAM SUTHERLAND (*Phil. Mag.*, 1897, [v], 44, 493—498).—The reasons usually assigned for the fact that the laws of the osmotic pressure of a solute in a solvent are the same as if the solvent were annihilated and the solute left as a perfect gas, are quite inadequate, because they would apply to any selected lot of the molecules of a solvent, and therefore to all the molecules, with the result that the laws of a perfect gas would have

to hold for all fluids down to and in the liquid state (compare Speyers, *Abstr.*, 1897, ii, 247). The answer to the problem is to be found in a closer study of the semipermeable membrane. If we seek to picture to ourselves how a membrane allows water molecules to pass, but not sugar molecules, our simplest conception of its structure is that of a mesh, amidst the threads of which the water molecules are packed in such a manner as to give way before one another almost as in ordinary water, whilst the sugar molecules are held back by the mesh. Thus the mesh forms a solid or quasi-solid framework through which water can pass with high viscous resistance, whilst the sugar molecule is absolutely blocked. Now if the framework turns back the sugar molecules, it must take the force of their blows and shield the water molecules from them. If, then, we suppose a semipermeable membrane separating water and a dilute solution of sugar in water, the sugar molecules are to be regarded as replacing some water molecules, but their collisions on the water in the membrane are rendered inoperative by the shielding action of the framework, so that the water molecules in the membrane receive more impacts on the side of the pure water than on the side of the solution, and therefore water flows through the membrane, until in the solution there is enough excess of hydrostatic pressure established to compensate for the inoperative impacts of the sugar molecules; this inequality of pressure which can be hydrostatically balanced is the osmotic pressure.

If the number of sugar molecules per unit volume is n and their mean velocity v , and the number of times a unit plane is crossed in the same direction by molecules per second is $nv/6$, then, taking unit area on the surface of the semipermeable membrane in contact with the dilute sugar solution, each molecule in being turned back receives momentum $2mv$, so that the whole pressure taken by unit area of the meshes of the membrane is $nmv^2/3$. Thus for the osmotic pressure we find the same expression as for the gas pressure of the sugar molecules if the water were annihilated and the sugar remained as a perfect gas.

H. C.

Real and Apparent Freezing Points and the Freezing Point Methods. By MEYER WILDERMANN (*Phil. Mag.*, 1897, [v], 44, 459—486).—See *Abstr.*, 1896, ii, 290.

Expansion during the Dissolution of Ammonium Salts. II. Ethyl Derivatives. By HUGO SCHIFF and U. MONSACCHI (*Zeit. physikal. Chem.*, 1897, 24, 513—521).—The authors have extended their previous researches (*Abstr.*, 1897, ii, 89) to the ethyl derivatives of ammonium chloride, and have determined the expansion during the dissolution of ethyl-, diethyl-, triethyl-, and tetrethyl-ammonium chlorides. For all these salts, expansion occurs during aqueous dissolution; in a 65 per cent. solution of ethylammonium chloride, this expansion reaches 0.07 of the volume of the mixed constituents. The curves for specific gravity against concentration and expansion against concentration are given, those for the monoethyl derivative being seen to agree very closely with that for ammonium chloride itself. For tetrethylammonium chloride, a maximum expansion occurs when the concentration is about 50 per cent. The effect of dissolution in alcohol was only

examined in the case of diethylammonium chloride, and here a contraction occurred.

L. M. J.

Compressibility of Salt Solutions. By HENRI GILBAULT (*Zeit. physikal. Chem.*, 1897, 24, 385—440. Compare Abstr., 1892, 766).—For the determination of the compressibility at temperatures not far removed from that of the atmosphere, a modification of Cailletet's method was employed, the difference being the use of a gold-coated platinum wire inserted in the neck of the piezometer to indicate the contraction instead of gilding the interior of the piezometer itself. Researches with water and solutions of iron salts indicate the availability and accuracy of the method. For high temperatures, the author used a cylindrical tube immersed horizontally in a bath of glycerol, the pressures being in all cases taken with a hydrogen manometer. In order to extend the observations to temperatures approaching the critical values, experiments were made with solutions of benzoic acid and of borneol in ether, and of resorcinol in ethylic alcohol, and the critical data of the various solutions were therefore first determined, curves of critical temperature, and critical pressure, against molecular concentration being given. The mixture law of Pawlewski is not obeyed, since at low concentrations a small quantity of salt causes a relatively great alteration of the critical temperature or pressure, the curves becoming nearly perpendicular to the axis of concentration. The curves for the solutions of borneol and of benzoic acid are almost identical, so that the author concludes that the change of critical temperature is only dependent on the molecular concentration and not on the nature of the dissolved substance. Tables are first given for the volumes, at various pressures, of ether and ethereal solutions of benzoic acid at 139.5—212.1°, and of water and aqueous solutions of potassium iodide at 20°; and in all cases the compressibility decreases with increase of pressure. Van der Waals' expression is insufficient, and the author finds that the expression giving the best agreement with the experimental numbers is $v = -1/M.k \log(p - A) + Bp + C$ where A , B , C and k are constants at constant temperature. The calculated and observed values are found to agree well for pressures up to 250 atmospheres in the case of aqueous solutions at ordinary temperatures, and ethereal and alcoholic solutions near their critical temperatures.

The influence of temperature on the compressibility of ethereal and alcoholic solutions was next considered, and the author obtains the following expression for the compressibility coefficient,

$$\gamma = \frac{a - b + p/\pi}{(\theta - T)/T + d(p - \pi)/\pi}$$

where θ is the absolute critical temperature, π the critical pressure, and a , d , and b constants. This expression gives satisfactory agreement with the observed numbers for all the solutions examined. As the values a , b , and d are identical for solvent and solution, it is evident that the law of corresponding states applies to the solutions, since the compressibility depends only on the ratios p/π and θ/T . In the above case, the compressibility increases with the temperature, but with water at ordinary temperatures the reverse obtains, and the author finds the temperature of minimum mean compressibility (1—300 atms.) to be

about 63.5° . In the case of salt solutions at low concentrations, similar results are found, but at certain concentrations the compressibility remains practically constant over a considerable range of temperature. To investigate the effect of concentration, solutions of sodium chloride were employed; the compressibility decreases as the concentration increases, but the curve is not a straight line, being slightly convex to both axes. The author gives the term "molecular compressibility" to the volume decrease of the solution containing the same number of molecules as 100 grams of water; and assuming complete dissociation of the dissolved substance and the value 18 as the molecular weight of water, obtains the equation $(\log \mu_0 - \log \mu)d/a = k$ where μ_0 and μ are the molecular compressibilities of water and solution, d is the density, a the ion concentration, and k a constant dependent only on the nature of the dissolved substance. This constant appears to be connected with the molecular volume contraction on dissolution in much water, as the magnitudes of both constants are in the same order for a series of 18 salts examined, and a formula connecting the two constants is given.

L. M. J.

Equilibrium in Solutions with Three Components:— β -Naphthol, Picric Acid, and Benzene. By BASIL B. KURILOFF (*Zeit. physikal. Chem.*, 1897, 24, 441—467).—In the equilibrium of the above system, the following solid phases may occur, β -naphthol, picric acid, benzene, β -naphthol picrate, and benzene picrate; preliminary experiments indicated the absence of any ternary phase. The transition point of the β -naphthol picrate on the β -naphthol side is 111° , and on the picric acid side 116° , that of benzene picrate being 84.3° ; hence, representing the equilibrium as usual in the equilateral triangle, the isothermals above 116° are complete curves with the binary solid phase of the naphthol picrate. Between 111° and 84° , they form three portions corresponding with the phases β -naphthol, β -naphthol picrate, and picric acid, whilst below 84° the last portion corresponds with the phase benzene picrate. Three quintuple points occur where three solid phases co-exist, namely, (1) picric acid, β -naphthol picrate, and benzene picrate; (2) benzene picrate, β -naphthol picrate, and benzene; and (3) β -naphthol, β -naphthol picrate, and benzene, and the temperatures and composition of solution at these points are given with the complete isothermals at various different temperatures.

L. M. J.

[Formation and Changes of Solids.] By F. WALD (*Zeit. physikal. Chem.*, 1897, 24, 509—512).—In a paper on the formation and changes of solids, Ostwald states that, during a transition from a particular state to one of greater stability, the change is not necessarily to the most stable, but to the nearest (*Abstr.*, 1897, ii, 308). The author discusses this statement, and considers it is not based upon sufficient theoretical foundations to be given as a general law.

L. M. J.

Velocity and Rate of Recombination of the Ions of Gases exposed to Röntgen Radiation. By E. RUTHERFORD (*Phil. Mag.*, 1897, [v], 44, 422—440).—Air which has been exposed to Röntgen radiation preserves the power of discharging positive and negative

electrification a short time after the rays have ceased. The duration of the after-conductivity of air and other gases has been investigated, and from the data thus obtained, the velocity of the ions through various gases has been determined.

The following table gives the times, T , for the number of ions to fall to half their original number.

Gas.	T in seconds.	Conductivity. Air=1.
Hydrogen.....	0.65	0.5
Air	0.3	1
Hydrogen chloride	0.35	11
Carbonic anhydride.....	0.51	1.2
Sulphurous anhydride.....	0.45	4
Chlorine	0.18	18

There seems to be no close connection between the values of T and the conductivities, although, as a general rule, it may be taken that the value of T diminishes with increase of conductivity. The value of T for the same gas was found to depend largely on the intensity of the radiation; and the presence of finely-divided matter, liquid or solid, affects the duration of the after-conductivity.

The velocities of the ions were found to be independent of the amount of ionisation of the gas, and, with the exception of chlorine, to follow the inverse order of the densities. The velocity of the hydrogen ion through hydrogen is nearly four times as fast as the velocity of the oxygen ion in oxygen. The ions of sulphurous anhydride gave the slowest velocity, being only about one-tenth of that of hydrogen.

H. C.

Table of the Elements arranged with the Atomic Weights in Multiple Proportions. By HENRY WILDE (*Compt. rend.*, 1897, 125, 707).

[Boring Holes in Glass.] By H. JERVIS (*Chem. News*, 1897, 76, 211—212).—Holes may be bored in glass by making a stellate group of cross scratches with the point of a three-cornered file, and then working out the glass with the sharp corners of a newly-broken end of such a file, most conveniently fitted in a brace. In all cases the tool must be moistened with turpentine.

D. A. L.

Inorganic Chemistry.

Influence of Hygroscopic Substances on the Combination of Hydrogen and Oxygen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, 125, 675—679).—Hydrogen chloride has no appreciable influence on the combination of oxygen and hydrogen at 100° or at 280°. Boron fluoride seems to slightly retard combination, but this result is probably due to alteration in the surface of the glass, which is somewhat strongly attacked. Sulphurous anhydride is without

influence at 100° , but at 280° , although the volume of the hydrogen remains unchanged, a notable quantity of oxygen is absorbed, and alkali sulphates are formed from the alkalis in the glass.

In presence of sulphuric acid at 280° , all the hydrogen is absorbed, and part of the sulphuric acid is reduced. A small quantity of oxygen also disappears, probably because it combines with the sulphurous anhydride.

Phosphoric anhydride seems to be without influence on the combination of hydrogen and oxygen at any temperature up to 280° , and even at this temperature the absorption of the water as fast as it is formed has no marked influence on the rate of combination. (Compare Abstr., 1897, ii, 548.) C. H. B.

The Ammonia of the Atmosphere. By REINHOLD HEINRICH (*Ann. Agron.*, 1897, 23, 485—486; from *Ber. Landw. Versuchs-Stat. Rostock*, 1894, 2, 10).—The ammonia present in the air was absorbed by means of dilute hydrochloric acid in glass vessels 5 cm. high and 10 cm. in diameter, which were protected from rain. Ammonia was determined monthly. The greatest amount (4.061 milligrams) was found in June, the lowest (0.854 milligram) in February. Taking the different seasons, the amounts were: winter, 2.912; spring, 6.712; summer, 9.766, and autumn, 4.678 milligrams. The total amount for the year was 24.066 milligrams. N. H. J. M.

Preparation of Nitrogen Chloride. By W. HENTSCHEL (*Ber.*, 1897, 30, 2642. Compare Abstr., 1897, ii, 404 and 447).—Attempts to modify the method of preparing nitrogen chloride from ammonium chloride by substituting bleaching powder for sodium hypochlorite have hitherto been unsuccessful, owing to the liberation of gas from the solution. This difficulty is overcome by employing hydrochloric acid, which prevents evolution of gas. A 10 per cent. solution of nitrogen chloride in benzene is prepared in the following manner.

3000 c.c. of a solution of bleaching powder, containing 22.5 grams of active chlorine per 1000 c.c., is gently agitated in a stoppered flask of 5000 c.c. capacity, and cautiously treated with a 10 per cent. solution of hydrochloric acid until a portion of the solution no longer yields gas when mixed with excess of a 20 per cent. solution of ammonium chloride. About 300 c.c. of the dilute acid is usually required for this purpose, and when the proper quantity has been added, the liquid is treated with 300 c.c. of a 20 per cent. solution of ammonium chloride, and then vigorously agitated with 300 c.c. of benzene during 30 seconds, the liquid meanwhile being protected from light; the benzene is separated from the aqueous liquid, and transferred to a folded filter containing 20 grams of crushed calcium chloride.

M. O. F.

Action of Sulphur on Silicides. Production of Silicon. By GUILLAUME J. L. DE CHALMOT (*Amer. Chem. J.*, 1897, 19, 871—877).—The author finds that the combined silicon of the copper silicide previously described by him (Abstr., 1897, ii, 262), may be partially liberated by acting on it with sulphur; the action begins at 200 — 250° and may be completed at 270 — 280° . Cuprous or cupric

sulphide is produced according to the quantity of sulphur used, and a little silicon sulphide is also formed; above 300° , however, the latter is obtained in larger quantity. The percentage of free silicon in two alloys containing originally 19.21 and 1.22 per cent. was increased to 25.77 and 7.27 respectively, by heating with sulphur at temperatures below 290° .

Manganese silicide is much less readily attacked by sulphur; below 300° , there is practically no action, whilst at the boiling point of sulphur, although some silicon sulphide is formed, no free silicon is liberated.

Chromium silicide is not attacked by sulphur at 300° , but at 450° some action seems to occur, although no silicon is liberated.

Iron silicide containing 29.51 per cent. of combined, and no free, silicon is not attacked by boiling sulphur. E. W. W.

Metallic Carbides which are Decomposed by Water. By HENRI MOISSAN (*Ann. Chim. Phys.*, 1896, [vii], 19, 302—337).—A *résumé* of previous papers. Compare Abstr., 1894, ii, 450; 1896, i, 633; ii, 364, 419, 422, 423, 650. J. J. S.

Volatilisation of Refractory Substances. By HENRI MOISSAN (*Ann. Chim. Phys.*, 1896, [vii], 19, 133—144).—The whole of this work has been published previously. Compare Abstr., 1893, ii, 507, 532; 1894, ii, 42, and 1895, ii, 164. J. J. S.

Atomic Weights of Argon and Helium. By HENRY WILDE (*Compt. rend.*, 1897, 125, 649—651).—Under low pressures at -76° , and at 20 atmos., nitrogen does not yield the spectrum of argon, nor argon the spectrum of nitrogen, even if the discharge is continued for several hours.

The author discusses the possible positions of argon and helium in his systematic arrangement of the elements according to their atomic weights. C. H. B.

Lithium Chloride Solutions. By GEORGES LEMOINE (*Compt. rend.*, 1897, 125, 603—605).—The sp. gr. at 0° of solutions of lithium chloride of various concentrations is as follows.

Weight of salt in 100							
grams of solution ...	4.26	12.18	22.2	32.5	41.4	43.2	
Sp. gr.	1.026	1.073	1.133	1.203	1.267	1.282	

These results are more accurately represented by two right lines, than by a continuous curve, and there seems to be a modification in the constitution of the solution from about 13 gram-molecules per litre to about 6 gram-molecules per litre, or from $\text{LiCl} + 3\text{H}_2\text{O}$ to about $\text{LiCl} + 8\text{H}_2\text{O}$.

The heats of dilution at 10° are as follows.

Gram-molecules of LiCl per litre	12	9	6	3	1	0.5	
Heat of dilution, starting from 12							
gram-molecules per litre	0	1.3	2.2	2.8	3.1	3.2	Cal.
Heat of dissolution taking 8.4 Cal. as							
maximum	5.2	6.5	7.4	8.0	8.3	8.4	„

There is no development of heat beyond $\text{LiCl} + 116\text{H}_2\text{O}$, and the results are practically the same at 20° as at 10° . The heat of dilution increases regularly with the quantity of water.

Lithium chloride and methylic alcohol :—

Temperature	1°	23°	50°
Ratio of the weight of salt to the weight of the saturated solution	0.267	0.27	0.30
Weight of salt in 100 grams of solution...	5.2	14.5	22.1
Sp. gr. at 21.5°	0.836	0.910	0.974
Sp. gr. at 0°	0.854	0.926	0.988
Gram-molecules of LiCl per litre	5	3	1
Molecules of MeOH per molecule of LiCl	4.7	7.9	24
Heat of dilution at 18° from 5 gram-mole- cules per litre.....	0	1.5	2.6
Heat of dissolution taking 10.9 as maximum	7.9	9.4	10.5
			3.0 Cal.
			10.9 Cal.

There is no development of heat beyond $\text{LiCl} + 48\text{MeOH}$.

Lithium chloride and ethylic alcohol.—Determinations of solubility gave

Temperature	1.6°	5.7°	13.0°	25.0°	40.6°	62.6°
Ratio of weight of salt to weight of its saturated solution	0.14	0.14	0.13	0.14	0.15	0.18

These results are represented by two right lines which intersect at a low angle, at a point corresponding with 30° , the more inclined portion leading slowly to the melting point of the salt. The solubility decreases, progressively in the order : water, methylic alcohol, ethylic alcohol, amyl alcohol.

Weight of salt in 100 grams of solution	5.2	10.1	14.6
Sp. gr. at 14.2°	0.839	0.871	0.903
Sp. gr. at 0°	0.851	0.881	—
Gram-molecules of LiCl per litre	3	2	1
Molecules EtOH per molecule LiCl	5.4	8.3	16.9
Heat of dilution from 3 gram-mols. per litre	0	—	2.1
Heat of dissolution taking 11.7 as maximum	9.1	—	11.2
			11.5 Cal.

C. H. B.

Colloidal Silver. By C. A. ALFRED LOTTERMOSER and ERNST VON MEYER (*J. pr. chem.*, 1897, 56, 241—247).—The authors propose to study quantitatively the action of various reagents on colloidal silver. They find that acids precipitate it from solution in the “molecular” state, time and dilution being of great importance; also with different acids widely different results are obtained, as is seen from the results of quantitative experiments already completed.

Colloidal silver is not precipitated by small amounts of sodium chloride or hydrochloric acid in presence of albumin. Apparently no silver albuminate is formed, but further details of these experiments, as also of those on the action of salts and the halogens on colloidal silver will be given subsequently.

A. W. C.

Calcium, Barium, and Strontium Borides. By HENRI MOISSAN and P. WILLIAMS (*Compt. rend.*, 1897, 125, 629—643).—Calcium boride is best obtained by heating an intimate mixture of 1000 parts of

calcium borate, 630 parts of aluminium and 200 parts of sugar carbon in a carbon crucible for 7 minutes with a current of 900 amperes and 45 volts. The aluminium completely reduces the calcium borate, whilst the carbon prevents the formation of aluminium oxide. The product is broken up and heated successively with dilute hydrochloric acid, boiling concentrated hydrochloric acid, water, ether, toluene, and hydrofluoric acid.

The calcium boride has the composition CaB_6 and forms transparent, microscopic cubic or rectangular crystals which scratch rock crystal, and even rubies; sp. gr. = 2.33 at 15° . It is not altered when heated to redness in hydrogen, is attacked by fluorine in the cold, with incandescence, by chlorine at a red heat, and also, but more slowly, by bromine and iodine. When heated in air, it does not burn below a bright red heat, and it is attacked by sulphur vapour under the same conditions. Nitrogen does not attack it even at 100° , and it is not decomposed by water under pressure at 250° , and even in a current of steam at higher temperatures decomposition is very slow. Gaseous halogen hydracids attack the boride at a dull red heat, but their solutions have no action on it; dilute sulphuric acid also does not attack it, but the concentrated acid is reduced. Ammonia is without action on the boride at the softening point of glass. On the other hand, oxidising agents, whether fused or in solution, attack it readily.

Strontium boride, SrB_6 , is obtained in a similar way and has similar properties, but is not attacked by fluorine in the cold; sp. gr. = 3.28 at 15° .

Barium boride, BaB_6 , is also obtained in the same way, and its properties are similar; it forms small but very regular crystals which scratch rubies, but not diamonds; sp. gr. = 4.36 at 15° . The yield of boride is greater than with calcium or strontium. C. H. B.

Basic Magnesium Salts. By TASSILLY (*Compt. rend.*, 1897, 125, 605—607).—Precipitated magnesium hydroxide yields no oxybromide when heated with solutions of magnesium bromide. If, however, 5 grams of magnesium oxide previously heated at a low temperature is added gradually to an almost boiling solution of 145 grams of magnesium bromide in 300 grams of water, and the solution is again heated, finally, to 150° , and then filtered and allowed to cool, the oxybromide, $\text{MgBr}_2 \cdot 3\text{MgO} + 12\text{H}_2\text{O}$ separates after about 15 days in small, acicular crystals which act on polarised light and show longitudinal extinction. When heated at 120° in dry air free from carbonic anhydride, the crystals lose $6\text{H}_2\text{O}$. The oxybromide alters when exposed to air, and absorbs carbonic anhydride; it is decomposed by water, alcohol, and most other reagents.

No definite oxyiodide could be obtained under similar conditions.

C. H. B.

Zinc Hydroxide in Precipitation. By VERNON J. HALL (*Amer. Chem. J.*, 1897, 19, 901—912).—The author has studied the precipitation of zinc hydroxide by means of potassium hydroxide solution, with reference to its effect in carrying down chlorine. When used in the ratio $2\text{KHO} : \text{ZnCl}_2$, no chlorine is found in the precipitate, whereas with

$1\frac{1}{2}$ KHO, 7.4 per cent. of the total chlorine is obtained in the precipitate, and the quantity decreases as the proportion of potassium hydroxide is diminished. When the ratio is 5—8KHO:ZnCl₂, no chlorine is carried down. Experiments made on precipitation in presence of potassium sulphate led to results similar to those obtained in the case of the precipitation of ferric hydroxide (Abstr., 1897, ii, 408). Increase of concentration tends to diminish the quantity of zinc precipitated and to increase the quantity of chlorine in the precipitate, whereas in the case of ferric hydroxide both the quantity of ferric oxide and chlorine in the precipitate decrease with increased concentration; in both cases, however, rise of temperature greatly reduces the quantity of metallic oxide and chlorine thrown down. E. W. W.

Impurities in Crude Copper. By FRÉDÉRIC SCHLAGDENHAUFFEN (*Compt. rend.*, 1897, 125, 573—574).—When water is allowed to remain in contact with filings of crude English or Chili copper for several days, it yields a yellow precipitate if acidified with hydrochloric acid and treated with hydrogen sulphide, the precipitate being more abundant if the copper and water are heated at 100°. If the same filings are afterwards treated with potassium hydroxide solution or dilute hydrochloric acid, both arsenic and antimony are found in the solution. Further, if the filings are heated in a current of carbonic anhydride, a mixture of arsenic and antimony oxides sublimes. Some other specimens of crude copper gave a sublimate which contained selenium, whilst one specimen gave a sublimate of lead sulphide in cubical crystals.

C. H. B.

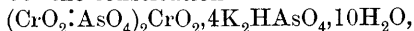
Solubility of Lead in Ammonia. By HERMANN ENDEMANN (*Amer. Chem. J.*, 1897, 19, 890—893).—Strong ammonia does not dissolve litharge, although Karsten states that lead dissolves in ammonia, forming a dark yellow solution. If lead be immersed for a day in strong ammonia solution (29 per cent.), there is no apparent change, but the solution contains some lead; if left for a longer time, the lead becomes coated with an orange, and later with a rust-coloured, precipitate, whose dark colour quickly fades if the precipitate is detached from the metal. After three days, the ammonia contains 0.0139 per cent. of lead, and if the action be allowed to continue for weeks, a white precipitate, which appears to be lead hydroxide mixed with oxides of other metals, is formed on the bottom and sides of the vessel. After drying, this precipitate contains only 0.15 per cent. of ammonia. Weak ammonia solution (2.9 per cent.) brings about a more rapid oxidation, for in 24 hours a white precipitate is formed on the glass, and on the surfaces of the liquid and the lead, and during the next 48 hours it rapidly increases in amount. The bearing of these observations on the manufacture of ammonia solution in lead-lined tanks, and the contamination of potable waters, is briefly discussed.

E. W. W.

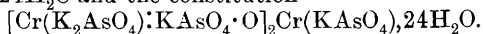
Researches on Aluminium. By HENRI MOISSAN (*Ann. Chim. Phys.*, 1896, [vii], 19, 337—356).—A *résumé* of work previously published. Compare Abstr., 1894, ii, 450; 1895, ii, 226; 1896, ii, 301, 338 and 601.

J. J. S.

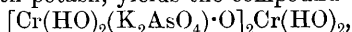
Chromium Arsenate. By N. TARUGI (*Gazzetta*, 1897, 27, ii, 166—175).—Schweitzer ascribed the composition, $K_8Cr_3As_6O_{28}, 20H_2O$, to the compound obtained by treating potassium chromate with arsenious acid. The author considers that, at ordinary temperatures, the salt has the constitution $[Cr(OH)_4 \cdot AsO_4]_2Cr(OH)_4, 4K_2HASO_4, 12H_2O$, after heating at 60° the constitution



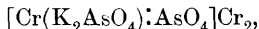
whilst by heating at 120° the $10H_2O$ is expelled; these constitutions are assigned on the basis of determinations of water of crystallisation. The compound of the composition $K_8Cr_3As_6O_{30}H_4$, obtained at 120° , is a green powder which, when boiled with potash, yields a pale green substance of the composition $K_4Cr_3As_2O_{16}, 12H_2O$, to which the constitution $(K_2AsO_4 \cdot CrO_2 \cdot O)_2CrO_2$ is assigned; when boiled with potassium hydrogen arsenite solution, it yields a substance of the composition $K_7As_5Cr_3O_{22}, 24H_2O$ and the constitution



This, on boiling with potash, yields the compound



which on heating at 150° is converted into a compound of the constitution $[CrO(K_2AsO_4 \cdot O)]_2CrO$; on treating the latter with potassium hydrogen arsenite, it yields a substance of the constitution



which is readily oxidised by potassium ferricyanide with formation of chromium arsenite, $AsO_4 \cdot Cr \cdot AsO_4 \cdot Cr \cdot AsO_4 \cdot Cr \cdot AsO_4$, as a dark green powder.

W. J. P.

Stannic Acids. By RODOLPHE C. ENGEL (*Compt. rend.*, 1897, 125, 651—654).—The author gives a *résumé* of the recorded observations concerning stannic and metastannic acids, and of the results of his own investigations (Abstr., 1897, ii, 376, and this vol., ii, 29).

C. H. B.

Action of Nitric Acid on Tin. By RODOLPHE C. ENGEL (*Compt. rend.*, 1897, 125, 709—711).—The white product of the action of nitric acid on tin has been variously described as stannic acid (Gay Lussac), metastannic acid (Berzelius, Fremy), stannic nitrate (Montemartini), and basic stannic nitrate (Walker). The author finds that the nature of the product depends on the conditions under which it is formed. If nitric acid of sp. gr. 1.42 is diluted with different proportions of water, kept at 0° , and a stick of tin immersed in 200 c.c. of the liquid, the products are (a) with 1 vol. of nitric acid and 2 vols. or more of water, stannous nitrate; (b) with equal volumes of water and acid, stannic nitrate, the liquid finally becoming syrupy; and (c) with undiluted acid, stannic nitrate, which, however, is precipitated, because it is insoluble in moderately concentrated nitric acid.

Stannic nitrate is, however, readily decomposed by water or by a rise of temperature, the first product being stannic acid mixed with a small proportion of metastannic acid, the proportion of the latter increasing, however, if the substance remains in contact with water, or if it is dried. The limiting compound in the cold is metastannyl stannate.

When metastannyl stannate is boiled with water, the conversion

into metastannic acid proceeds further, and parastannic acid is also formed in gradually increasing quantity (this vol., ii, 29). Pure metastannic acid yields parastannic acid when boiled with water; the latter may perhaps be regarded as an internal anhydride of the former. Metastannic acid is not formed by the direct action of nitric acid on tin; the substance described by Berzelius was in reality parastannic acid.

C. H. B.

Mineralogical Chemistry.

Native Iron in the Coal Measures of Missouri. By EUGENE T. ALLEN (*Amer. J. Sci.*, 1897, [iv], 4, 99—104).—Very few well-authenticated occurrences of terrestrial iron, which may not possibly be artificial or meteoric, have been described. It has been stated to be found in igneous rocks, in river sands, and in connection with carbonaceous matter. Analysis I is of native iron from a boring in sandstone (containing 30.90 per cent. of calcareous cement and 1.27 per cent. Fe_2O_3) at Cameron, Clinton Co. The iron occurs in irregular fragments weighing on an average 0.5 gram, the largest weighing 45.4 grams; it is soft ($H=4$), very malleable, and on the fresh fracture almost silver-white. A well-marked, laminated cleavage is present, but no Widmanstätten figures are brought out by etching. Analysis II is of pieces of iron from a grey clay (containing 79.32 SiO_2 and 1.67 Fe per cent.) in a boring passing through sandstone and lignite at Weaubleau, Hickory Co. III is of iron from fire-clay (containing 65.25 SiO_2 and 3.62 Fe per cent.) in a boring, passing through a coal bed, at Holden, Johnson Co.

	Fe.	SiO_2 .	C.	P.	Cu, Ni, Co.	Sp. gr.
I.	99.16	0.37	0.065	0.207	Nil	7.63—7.73, 7.43
II.	99.39	0.31	not det.	0.13	—	7.58, 7.83, 7.88
III.	97.10	1.65	not det.	0.176	—	7.49

These specimens of iron, when first extracted from the matrix, are tarnished, but are free from rust; they are very soft, and contain no nickel. The depth (35—51 feet) at which they occur excludes the possibility of meteoric origin; their occurrence in coal measures is suggestive of reduction.

L. J. S.

Composition of Pre-Carboniferous Coals. By W. HODGSON ELLIS (*Chem. News*, 1897, 76, 186—188).—In anthraxolite from five different localities, the percentage of ash ranged between 0.72 and 48.37, whilst the extreme variations in the percentage of the other constituents, calculated on the dry, and ash-free substance, were: carbon, 90.5 and 97.1; hydrogen, 0.5 and 6.2; oxygen, 1.6 and 5.5, which numbers support the view that anthraxolites result from the metamorphosis of bitumen.

D. A. L.

Identity of Andorite, Sundtite, and Webnerite. By GEORGE T. PRIOR and LEONARD J. SPENCER (*Min. Mag.*, 1897, 11, 286—301; and *Zeits. Kryst. Min.*, 1898, 29).—Andorite was described in 1892 as

an orthorhombic mineral from Felsőbánya, Hungary, having the composition $2\text{PbS}, \text{Ag}_2\text{S}, 3\text{Sb}_2\text{S}_3$ (Abstr., 1895, ii, 21). Sundtite from Oruro, Bolivia, was shortly afterwards described as being orthorhombic, with the formula $(\text{Ag}_2, \text{Cu}_2, \text{Fe})\text{S}, \text{Sb}_2\text{S}_3$ (Abstr., 1893, ii, 382). Webnerite, also from Oruro, was described as an argentiferous zinckenite with the composition $2\frac{1}{2}(\text{PbS}, \text{Sb}_2\text{S}_3) + \text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$ (Abstr., 1895, ii, 170). A new analysis of *measured crystals* from the original sundtite specimen gave the results under I, agreeing closely with the formula $2\text{PbS}, \text{Ag}_2\text{S}, 3\text{Sb}_2\text{S}_3$, and thus showing, when considered in connection with the crystallographic measurements, the identity of sundtite with andorite. Measurement of a rough crystal from the original specimen of webnerite also proves the identity of this mineral with andorite. The results of the original analysis of webnerite agree just as closely with the more simple formula $2\text{PbS}, \text{Ag}_2\text{S}, 3\text{Sb}_2\text{S}_3$ as with the formula given above, especially when the copper is taken as replacing silver.

	Pb.	Ag.	Cu.	Fe.	Sb.	S.	Total.	Sp. gr.
I.	24·10	10·94	0·68	0·30	41·31	22·06	99·39	5·377
II.	21·81	11·73	0·73	1·45	41·76	22·19	99·67	5·33

A description is also given of andorite "from Hungary," which occurs with quartz, pyrites, fluorite, chalybite, &c., in small crystals closely resembling freieslebenite in appearance; analysis of measured crystals gave the results under II. Alunite and cassiterite are described as being associated with Bolivian andorite.

The characters of andorite are summarised as follows: orthorhombic with $a : b : c = 0·6771 : 1 : 0·4458$; the number of observed crystal forms is 42. Colour, dark steel-grey, with brilliant, metallic lustre; opaque. Streak black and shining; powder dull. There is no cleavage, and the fracture is smooth and conchoidal; brittle. Sp. gr. = $5·35$; $H = 3\frac{1}{4}$. Since there is no crystallographic relationship between andorite and the orthorhombic zinckenite ($\text{PbS}, \text{Sb}_2\text{S}_3$), and the monosymmetric miargyrite ($\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$), it is pointed out that andorite must be a double salt, $2(\text{PbS}, \text{Sb}_2\text{S}_3) + \text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3 = \text{PbAgSb}_3\text{S}_6$. L. J. S.

[Stannite from Bolivia.] By ALFRED W. STELZNER (*Zeit. deutsch. geol. Ges.*, 1897, 49, 97, 131).—In a paper (pp. 51—142) on the silver-tin ores of Bolivia, it is pointed out that the mode of occurrence of cassiterite in Bolivia is quite different from that in other parts of the world, where it occurs in association with boron and fluorine minerals at granite contacts. In Bolivia, on the other hand, it occurs in ordinary mineral veins with sulphide ores, and is sometimes associated with stannite and other sulphostannates.

At Potosi, stannite occurs with pyrites, tetrahedrite, and mispickel in cubic crystals with tetrahedral development; the colour is steel-grey with a yellowish tinge, and the streak is black. Analysis by E. Ziessler of massive material, containing some blende and pyrites, gave, after deducting 6·96 per cent. of gangue,

S.	Cu.	Sn.	Fe.	Zn.	Ge.	Total.	Sp. gr.
29·00	29·00	27·50	13·75	0·75	nil	100·00	4·495

Heated in a closed tube, it decrepitates and gives off much sulphur in which it differs from ordinary stannite. L. J. S.

Distribution of Titanic Oxide upon the Earth. By FRANCIS P. DUNNINGTON (*Chem. News*, 1897, **76**, 221—222. Compare Abstr., 1892, 791).—Titanic oxide has been found in 34 samples of soil from various parts of the world and also in the borings from a deep well extending to a depth of 4490 ft. The quantity varied from 2·33 to 0·09 per cent. in the air-dried soil, the average being 0·515 per cent. when the exceptionally rich sample (from St. Helena) containing 2·33 per cent. is omitted. D. A. L.

Composition of Ilmenite. By SAMUEL L. PENFIELD and H. W. FOOTE (*Amer. J. Sci.*, 1897, [iv], **4**, 108—110; and *Zeit. Kryst. Min.*, 1897, **28**, 596—597).—The formula of ilmenite has been written as $(\text{Fe}, \text{Mg})\text{O}, \text{TiO}_2$ and as $(\text{Fe}, \text{Ti})_2\text{O}_3$. The mineral crystallises in the rhombohedral-tetartohedral division of the hexagonal system and the length of the vertical axis, 1·385, is not between those of hæmatite (1·359) and artificial titanium sesquioxide (1·316), neither of which show the tetartohedrism of ilmenite; this, together with the fact that the amount of Ti_2O_3 never exceeds that of Fe_2O_3 , tells against the isomorphous mixture as given in the second formula. The presence of magnesia in many ilmenites can also not be accounted for by this formula. The largest amount of magnesia found in any ilmenite is shown in Rammelsberg's analysis of material from Warwick, New York, but as this has been suggested to be due to impurities, two new analyses have been made of a crystal from this locality; the mean is

SiO_2 .	TiO_2 .	FeO .	MgO .	MnO .	Fe_2O_3 .	Total.	Sp. gr.
0·37	57·29	24·15	15·97	1·10	1·87	100·75	4·345

Here the ratio $\text{RO}_2:\text{RO}$ is very close to 1:1, thus indicating the existence of the molecule RO, TiO_2 . Since $\text{Fe}_2\text{O}_3 + \text{Ti}_2\text{O}_3 = 2\text{TiO}_2 + 2\text{FeO}$, it cannot be told by chemical means whether all the titanium exists as TiO_2 , but as MgO, TiO_2 is present it is best to assume that FeO, TiO_2 is also present, and not $(\text{Fe}, \text{Ti})_2\text{O}_3$. In the published analyses of ilmenite, where $\text{TiO}_2:\text{RO} = 1:1$, there is often an excess of Fe_2O_3 , and it is reasonable to suppose that the hæmatite molecule, Fe_2O_3 or FeFeO_3 , is capable of mixing with the ilmenite molecules, FeTiO_3 and MgTiO_3 , just as calcite and sodium nitrate are practically isomorphous. L. J. S.

Bixbyite a New Mineral. By SAMUEL L. PENFIELD and H. W. FOOTE (*Amer. J. Sci.*, 1897, [iv], **4**, 105—108; and *Zeit. Kryst. Min.*, 1897, **28**, 592).—Bixbyite was found by M. Bixby in cubic crystals implanted on topaz and decomposed garnet and rhyolite at about 35 miles south-west of Simpson, in Utah. The cubes are occasionally modified by the trapezohedron {211}. The colour is brilliant black with metallic lustre, and the streak is black. $H = 6-6\cdot5$; sp. gr. = 4·945. The mineral fuses at about 4 and becomes magnetic. The fine powder is difficultly soluble in hydrochloric acid, and from the amount of chlorine evolved the available oxygen was calculated. The mean of two very close analyses is

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	TiO_2 .	MnO .	MgO .	Available O.	Total.
1·21	2·53	47·98	1·70	42·05	0·10	4·38	99·95

The silica and alumina are due to the presence of topaz. Two formulæ

are possible, Fe_2O_3 , Mn_2O_3 and FeO , MnO_2 . If the mineral is an isomorphous mixture of Fe_2O_3 , Mn_2O_3 and Ti_2O_3 , as in the first formula, it would be expected to be rhombohedral and to belong to the hæmatite group. The second formula, which shows a relation to the cubic perovskite, $(\text{CaO}, \text{TiO}_2)$, is the one adopted; small quantities of MgO and MnO replace FeO , and there is a little TiO_2 with the MnO_2 . The mineral is therefore to be regarded as a ferrous salt of manganous acid, H_2MnO_3 , corresponding with the manganese salt, braunite, MnMnO_3 .

The associated topaz is crystallographically described; it is sometimes opaque owing to the enclosure of minute quartz crystals.

L. J. S.

Composition of Hamlinite. By SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1897, [iv], 4, 313—316; and *Zeit. Kryst. Min.*, 1897, 28, 588. Compare Abstr., 1891, 20).—Hamlinite was described in 1890 as rhombohedral crystals occurring with herderite and bertrandite at Stoneham, Maine; only a few small crystals were found, so an analysis was not possible. The mineral has now been found with apatite, herderite, and bertrandite on felspar and muscovite in Oxford Co., Maine. The small crystals are rhombohedral or prismatic in habit; $r:r' = 88^\circ 41'$. For the analysis, a whole specimen was powdered and the hamlinite separated by a heavy liquid, the accompanying apatite was then dissolved in dilute acid; the hamlinite so obtained, of sp. gr. 3.159—3.283, when examined under the microscope, appeared to be pure. The mean of four partial analyses is

P_2O_5 .	Al_2O_3 .	Fe_2O_3 .	SrO.	BaO.	H_2O .	F.	SiO_2 .	K_2O .	Na_2O .	Total (less) O for F.
28.92	32.30	0.90	18.43	4.00	12.00	1.93	0.96	0.34	0.40	99.37

Deducting silica, alkalis, &c., as felspar and mica, this agrees closely with the formula $\text{Al}_3\text{Sr}(\text{OH})_7\text{P}_2\text{O}_7$, or $[\text{Al}(\text{OH})_2]_3(\text{SrOH})\text{P}_2\text{O}_7$, in which strontium and hydroxyl are partly replaced by barium and fluorine respectively. This is the first mineral pyrophosphate that has been described, neither has a phosphate of strontium or barium been before observed. The associated bertrandite is crystallographically described.

L. J. S.

Monazite from Idaho. By WALDEMAR LINDGREN (*Amer. J. Sci.*, 1897, [iv], 4, 63—64).—The gravels and sands of the gold placers in the granite area of "Idaho Basin" contain, in the heavy residues, ilmenite, zircon, garnet, and monazite; the monazite is present in considerable quantity as yellowish or brownish grains. The crude material, with about 70 per cent. of monazite, contains about 48 per cent. of cerium oxides, and 1.20 per cent. of thorium.

L. J. S.

Tripuhyite, a New Antimonate of Iron from Brazil. By EUGEN HUSSAK and GEORGE T. PRIOR (*Min. Mag.*, 1897, 11, 302—303).—This new mineral is found as dull, greenish-yellow fragments in association with lewisite (Abstr., 1895, ii, 508) and derbylite (Abstr., 1897, ii, 410) in the cinnabar-bearing gravels at Tripuhy, Minas Geraes. Thin sections show an aggregate of translucent, highly refractive, and strongly doubly-refracting grains, which are biaxial and of a bright

canary-yellow colour. A few minute flakes, probably of muscovite, is the only impurity present. The streak is canary-yellow. When heated, the mineral is infusible, and gives off antimony fumes, leaving a residue of ferric oxide. It is insoluble in hydrochloric and nitric acids. Sp. gr. 5·82. Analysis gave

Sb ₂ O ₅ .	FeO.	CaO.	SiO ₂ .	Al ₂ O ₃ .	TiO ₂ .	Undet. (alkalis?).	Total.
66·68	27·70	0·82	1·35	1·40	0·86	(1·19)	100·00

Assuming the iron to be ferrous, this agrees with the formula 2FeO, Sb₂O₅. L. J. S.

Blödite from the Punjab Salt Range. By FREDERICK R. MALLET (*Min. Mag.*, 1897, 11, 311—317).—Good crystals of blödite occur in the salt beds at the Mayo mines and at the Varcha mine; in external form and optical characters, they agree closely with the Stassfurt mineral. The crystals are colourless and usually transparent, but are sometimes clouded by fluid inclusions. The mean of two analyses is

MgO.	Na ₂ O.	SO ₃ .	H ₂ O.	NaCl.	Total.
11·97	18·53	47·82	21·54	0·07	99·93

This agrees closely with the usual formula, MgSO₄.Na₂SO₄ + 4H₂O. Between 85° and 120°, it loses 2H₂O, and the remainder begins to go off at about 125°. Blödite has probably been formed by the interaction of magnesium sulphate (kieserite) with rock salt. L. J. S.

[**Cupro-scheelite from New South Wales.**] By GEORGE W. CARD (*Records Geol. Survey N.S.W.*, 1897, 5, 122).—Cupro-scheelite occurs, associated with bornite and copper carbonates, at Upper Timby, near Yeoval. It is usually of a greenish tint, but is sometimes white, and has a waxy appearance; rectangular outlines can be distinguished. Analysis gave

WO ₃ .	MoO ₃ .	CaO.	MgO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	CuO.	CO ₂ .	H ₂ O.	Gangue.	Total.
57·73	trace	14·40	0·22	2·98	trace	7·08	1·56	2·55	13·04	99·56

Deducting gangue, this corresponds with WO₃, 66·7; CuO, 8·18 per cent. Stolzite from Broken Hill is also described. L. J. S.

Apophyllite from South Africa. By J. A. LEO HENDERSON (*Min. Mag.*, 1897, 11, 318—322).—In the so-called “blue-ground” of the farm Koppiesfontein near Jagersfontein, Orange Free State, apophyllite occurs as embedded octahedral crystals showing only the form $p\{111\}$. The crystals are almost colourless or feebly yellow; sp. gr. 2·371. Cleavage flakes show in polarised light a division into four sectors with biaxial characters. Analysis by Röhrig gave the results under I. No fluorine is given off when the mineral is treated directly with sulphuric acid, but it may be obtained from the ammonia precipitate of the hydrochloric acid solution of the mineral (compare Abstr., 1896, ii, 369).

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	F.	NH ₃ .	Total.
I.	51·16	1·60	—	25·44	0·29	3·35	0·43	16·73	1·04	0·11	—	100·15
II.	34—35	15·44	3·55	14·80	10—11	7·16	—	—	11·34	—	—	—

The occurrence of apophyllite as embedded crystals is somewhat unusual; the matrix is a soft, talcose, serpentine-like mass, which gave the results under II; it is compared with the Kimberley "blue-ground."
L. J. S.

Pseudomorphs from Northern New York. By CHARLES HENRY SMYTH, JUNR. (*Amer. J. Sci.*, 1897, [iv], 4, 309—312).—Pseudomorphs of pyroxene after wollastonite occur at Diana, Lewis Co.; here there has been an addition of magnesia. The crystals of scapolite and pyroxene in the limestone of Gouverneur, St. Lawrence Co., are sometimes altered to aggregates of a brown mica, probably phlogopite. Cases are cited in which garnet and epidote are apparently the alteration products of scapolite.
L. J. S.

Serpentines of Davos. By JOHN BALL (*Inaug. Diss. Zürich*, 1897, 47 pp.).—As shown by its mode of occurrence and by the results of contact-metamorphism, the serpentine of Davos in Switzerland has been derived from a lherzolite which was intruded into the surrounding gneisses, dolomites, and schists. In the least altered rock (anal. I), olivine, enstatite and diallage are present, together with picotite, accessory rutile, and rarely hornblende. The most altered rock from the margins of the mass gave analysis II. White steatite (anal. III) occurs in lenticular patches and veinlets in the schists near the serpentine. Opicalcite from the calcareous schists at the serpentine contact gave IV; it consists of fragments of altered serpentine with secondary hornblende in a calcite matrix.

	SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.	CO ₂ .	Total.	Sp. gr.
I.	41·83	5·46	0·45	1·13	2·73	2·26	34·64	10·54	—	99·04	2·78
II.	39·95	1·86	0·23	3·37	3·57	—	35·63	13·87	—	98·48	2·61
III.	63·96	—	—	—	2·03	—	29·51	5·34	—	100·84	—
IV.	32·96	3·15	—	3·26	1·90	12·76	28·71	8·26	8·69	99·69	2·73

The associated rocks are described in detail; these are schistose whilst the serpentines are shattered.
L. J. S.

[Leucite Rocks in Wyoming.] By WHITMAN CROSS (*Amer. J. Sci.*, 1897, [iv], 4, 115—141).—It was in the Leucite Hills, in southwestern Wyoming, that leucite was first discovered in America, in 1871; here there is a lava flow of leucite rock, of which two new types are distinguished and named wyomingite and ordenite.

Wyomingite is a compact, reddish-grey rock with a marked schistose structure owing to the parallel arrangement of small, reddish flakes of mica, this being the only mineral visible in hard specimens. Under the microscope, it is seen to consist of phlogopite flakes in a ground-mass of small leucite crystals and diopside microlites; apatite, biotite, and residual glass are also present in small amount. From analysis I, the mineralogical composition is calculated as

Free silica.	Leucite.	Noselite.	Diopside.	Phlogopite.	Accessories.
18·7	26·1	8·7	18·8	19·9	7·8

The presence of so large an excess of silica is difficult to explain, since there is no quartz, &c., to be seen in the thin sections.

Ordenite (anal. II) has, with the exception of a vesicular structure

the same outward appearance as wyomingite; here leucite and sanidine predominate as compared with phlogopite, diopside, and a peculiar amphibole; apatite and biotite are also present in small amount.

Madupite (anal. III) is the name given to a rock, probably a lava, from Pilot Butte, 15 miles east of the Leucite Hills; it is a dull, felsitic-looking rock with numerous reddish specks of phlogopite. Under the microscope are seen diopside, phlogopite, and probably perovskite in a brownish, glassy base. As calculated from the analysis, this base has the composition of leucite.

Phlogopite from wyomingite gave analysis IV, and V is of diopside from wyomingite and madupite. The rock analyses (I—III) by W. F. Hillebrand are interesting, on account of the large number of determined constituents. In connection with these rocks, the classification of leucite rocks is discussed.

	SiO ₂ .	TiO ₂ .	ZrO ₂ .	Al ₂ O ₃ .	(Ce,Di) ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	SrO.	BaO.
I.	50.23	2.27	—	11.22	0.03	0.10	3.34	1.84	0.05	5.99	0.24	1.23
II.	54.17	2.67	0.22	10.16	—	0.05	3.34	0.65	0.06	4.19	0.18	0.59
III.	42.65	1.64	—	9.14	0.11	0.07	5.13	1.07	0.12	12.36	0.33	0.89
IV.	42.56	2.09	—	12.18	—	0.73	2.73	0.90	—	0.20	—	1.00
V.	50.86	3.03*	—	nil	—	—	1.19	1.82	0.03	23.32	—	—

	MgO.	K ₂ O.	Na ₂ O.	Li ₂ O.	H ₂ O (at 110°).	H ₂ O (above 110°).	P ₂ O ₅ .	SO ₃ .	Cl.	F.	CO ₂ .	Total (less O for F).	Sp.gr.
I.	7.09	9.81	1.37	trace	0.93	1.72	1.89	0.74	0.03	0.50	—	100.40	2.779
II.	6.62	11.91	1.21	„	0.52	1.01	1.59	0.16	0.06	0.36	0.49	100.04	2.699
III.	10.89	7.99	0.90	„	2.04	2.18	1.52	0.58	0.03	0.47	—	99.91	2.857
IV.	22.40	10.70	0.44	„	2.35	—	0.06	—	—	2.46	—	99.77	—
V.	17.42	0.42	0.76	—	0.31	—	—	—	—	—	—	99.16	3.290

* TiO₂ + P₂O₅. II contains a trace of nickel.

Nitre (anal. VI, by L. G. Eakins) and nitratine (anal. VII) occur as crusts in exposed cavities in these rocks. These minerals are possibly of volcanic origin, as is sal ammoniac at Vesuvius.

	K ₂ O.	Na ₂ O.	N ₂ O ₅ [calcd.].	CaO.	SO ₃ .	H ₂ O.	NaCl.	Total.
VI.	44.91	—	[51.49]	1.09	1.59	0.63	0.16	99.87
VII.	4.97	32.09	[61.58]	0.24	0.33	0.68	trace	99.89

L. J. S.

Mineral Water from Buda. By LUDWIG ILOSVAY DE NAGY ILOSVA (*Földtani Közlöny*, 1896, 26, 293—300).—Water from the Mathias Hunyady spring, No. III, near Buda, in Hungary, gave the following results on analysis. It is colourless, and has a slight alkaline reaction and a bitter taste. Sp. gr. 1.03295 at 20°. In parts per 1000: SiO₂, 0.0109; Fe₂O₃.Al₂O₃, traces; Mg, 3.0033; Na, 5.3993; K, 0.3511; Ca, 0.4136; SO₄, 22.3805; Cl, 1.3119; HCO₃, 0.6846 = 33.5552; free CO₂, 0.0335. This is compared with other bitter waters from the neighbourhood of Buda; those nearer the town contain more chlorine.

L. J. S.

Physiological Chemistry.

Length of Time during which Food remains in the Digestive Apparatus of Rabbits. By HUGO WEISKE (*Landw. Versuchs-Stat.*, 1897, 48, 375—379).—Six rabbits of the same litter, about four months old, received, for 12 days, 60 grams of air-dried oats; they were then fed on hay *ad libitum*, killed at different intervals, and the contents of their stomachs examined. The first was killed 3 hours after feeding with hay commenced, the second 6 hours, the third, fourth, fifth and sixth, 9, 12, 24 and 48 hours respectively after the commencement of hay feeding. The results showed that, under the conditions of the experiment, the grain was sufficiently digested in about two days to enable the excrement to be collected for the purpose of feeding experiments on the utilisation of foods. N. H. J. M.

Effect of Increasing Amounts of Fat in Food on the Utilisation of the Food Constituents. By A. WICKE and HUGO WEISKE (*Landw. Versuchs-Stat.*, 1897, 48, 390—400).—Two sheep were fed for 24 days as follows. No. 1 received during the whole period 1 kilogram of hay and 0.25 kilogram of linseed cake per day, whilst No. 2 received 0.75 and 0.2 kilogram of hay and cake respectively. For the first week no other food was given, but during the second, third, and fourth periods of the experiment, No. 1 had 60, 120, and 180 grams of olive oil, and No. 2, 50, 100, and 150 grams of olive oil per day. The results are given in tables showing the amounts of dry matter, proteid, fat, crude fibre, &c., in the food and in the fæces, and the amounts (actual and per cent.) digested.

Even in the fourth period, when the amount of oil given was very large, the oil was mostly digested and resorbed; and the digestibility of the fat of the food, and also, but to a less extent, the dry matter of the food, was increased. The digestibility of the proteids remained about the same, whilst the digestibility of the crude fibre was increased, and that of the nitrogen-free extract substances diminished, under the influence of oil. On the whole, however, the results showed that large amounts of oil have no great effect on the digestibility and resorption of food constituents. N. H. J. M.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation without Yeast Cells. By EDUARD BUCHNER and RUDOLF RAPP (*Ber.*, 1897, 30, 2668—2678. Compare Abstr., 1897, ii, 380).—The authors are convinced that the yeast extract described in previous papers does not owe its fermentative properties to micro-organisms, because passage through a Chamberland filter, which arrests bacteria, does not impair its activity. Moreover, it is

found that a specimen of the extract, which time has rendered powerless to ferment, acquires but feeble activity when treated with 1 gram of living yeast, and becomes quite inactive if potassium arsenite is also added, whereas a freshly prepared extract rapidly induces fermentation. If the fermentative capacity of the yeast extract is due to micro-organisms, it would be expected that the activity of the liquid would increase with lapse of time, owing to the reproduction of the agents; very rapid deterioration occurs, however, when the extract is kept for 2 days, when it loses the fermentative property. Zymase is not produced by quiescent yeast; a specimen of fresh yeast which yields an active extract when submitted at once to pressure, gives rise to an inactive liquid if pressed after an interval of 3 days. This circumstance probably affords an explanation of the previously observed fact that specimens of yeast from some breweries failed to yield an extract containing zymase.

The paper contains a description of the method by which the yeast extract is most conveniently obtained, and further observations have been made regarding the nature of its active enzyme, zymase. Its behaviour towards hydrocyanic acid resembles that of other enzymes, this agent checking the fermentative activity of zymase, and also destroying the power of the original yeast extract to cause effervescence when mixed with hydrogen peroxide.

Applying Meissl's method of determining the fermentative power of yeast, the authors have studied the fermentative power of yeast extract under various conditions; tables have been compiled which embody the results of their experiments on the influence of temperature, antiseptics, time, and the concentration of the sugar solution employed. Yeast extracts from different sources have been also compared.

M. O. F.

Oxidising Ferments (Oxydases). By GABRIEL BERTRAND (*Ann. Agron.*, 1897, 23, 285—399. Compare Abstr., 1896, i, 534; ii, 61 and 571; 1897, ii, 117, 338, 493; this vol., i, 53).—It was previously observed that the ash of laccase contains manganese. It is now shown that the activity of the laccase varies with the amount of manganese present. Three samples (each 0.2 gram) which, in presence of 50 c.c. of 2 per cent. quinol solution, absorbed in $1\frac{1}{2}$ hours 19.1, 15.5, and 10.6 c.c. of oxygen, contained respectively 0.159, 0.126, and 0.098 per cent. of manganese.

It was not found possible to remove the manganese from preparations of laccase, but by altering the mode of preparation the author was able to obtain a sample almost free from manganese. This sample, with quinol, absorbed only about 0.3 c.c. of oxygen, whilst the addition of manganese sulphate ($Mn = 0.001$ gram) induced an absorption of 4.3 c.c. of oxygen. Other sulphates (iron, aluminium, cerium, zinc, copper, calcium, magnesium, and potassium) had no effect.

Direct experiments with a number of manganese salts showed that they all had the property of fixing free oxygen in presence of quinol, although in very different degrees. Solutions were prepared containing quinol 1 per cent., and manganese 0.1 per cent. The solutions (100 c.c.) contained in 250 c.c. flasks were kept in agitation for a time,

and the amount of oxygen absorbed ascertained. The following numbers show the amounts of gas absorbed by each salt :

Nitrate.	Sulphate.	Chloride.	Formate.	Benzoate.
1.5	1.6	1.8	7.4	15.3
Acetate.	Salicylate.	Lactate.	Gluconate.	Succinate.
15.7	16.3	17.6	21.6	22.1

In some cases, a crystalline precipitate (quinhydrone) separated : with the gluconate in 2 hours, but much later with the salicylate.

N. H. J. M.

Vegetation with and without Argon. By TH. SCHLOESING, jun. (*Compt. rend.*, 1897, 125, 719—722).—Oats and feather-grass (*Houque laineuse*) respectively were grown in confined volumes of ordinary air and air deprived of argon, the ratio CO_2/O_2 being determined in each case, and the general appearance, behaviour, &c., of the plants observed. The conclusion drawn from the experiment is that argon has no appreciable influence on vegetation.

C. H. B.

Researches on Germination. By F. VICTOR JODIN (*Ann. Agron.*, 1897, 23, 433—471. Compare Giglioli, *Abstr.*, 1897, ii, 423).—Peas, kept under ordinary conditions, retain from 0.1 to 0.3 gram of water per gram of dry matter, an amount which is sufficient to determine gradual changes which finally result in loss of germinating power.

Peas (3.452 grams) kept in air over mercury and exposed to light, in $4\frac{1}{2}$ years absorbed 2.4 c.c. of oxygen, and produced 1.8 c.c. of carbonic anhydride ; the peas no longer germinated. In absence of light, there was no action during the same period, and the seeds germinated normally. Of nine peas which were kept immersed in mercury for over 10 years, two germinated almost normally ; two others germinated, but not satisfactorily, whilst the remaining five failed to germinate completely.

A number of peas, weighing 3.694 grams, were kept in air saturated with water at 20—23°. In 10 days, the weight of the seeds increased to 5.602 grams, but there was no germination. Thirteen days later, the weight increased to 6.143 grams, and 15 peas germinated, whilst six did not. No more of the peas germinated, and the weight, 37 days after the commencement of the experiment, was 5.650 grams. The results show that the minimum of hydration at which germination takes place is about 0.9 per grain of seed.

In the next experiments, sterilised peas were kept under glass shades closed with mercury, and the composition of the air ascertained from time to time. A few c.c. of sterilised water was present, to enable germination to take place. Similar experiments were made with peas with insufficient moisture for germination (hydration = 0.331 to 0.737). The results (which are given in detail in tables) show that the peas which could not germinate, owing to the amount of water present being insufficient, showed a respiratory activity, apparently similar to, and sometimes exceeding, that of the peas which germinated.

With regard to the effect of an excess of carbonic anhydride on germination, peas and cress did not germinate when kept in an atmosphere of $\text{CO}_2 = 58.3$, $\text{O}_2 = 26.6$, and $\text{N}_2 = 15.1$ per cent. After being 17 days in this atmosphere, all the peas were killed, but most of the

cross germinated when surrounded with ordinary air. Peas, however germinate in presence of 7 per cent. of carbonic anhydride, and produced, in 13 per cent. of the gas, rootlets 2—3 mm. long; in presence of 50 per cent. of carbonic anhydride, peas rapidly lose the power of germinating, although they absorb oxygen and give off carbonic anhydride.

The first stages of germination, resulting in the production of a rootlet 2—3 times the diameter of the pea, can take place without the intervention of an appreciable amount of oxygen. Subsequently, oxygen is necessary; the oxygen must be in the uncombined state, and is not available either in the form of nitrates or of hydrogen peroxide. The reduction of nitrates, during germination, observed by Boussingault was, no doubt, due to the action of microbes (*Agronomie*, 7, 130. Compare also Godlewski, *Abstr.*, 1897, ii, 583). N. H. J. M.

Influence of Arsenic on Germination. By BENGT JÖNSSON (*Ann. Agron.*, 1897, 23, 491; from *Konigl. Landt. Akad. Handl.*, 1896, 35, 95).—Lyttkens considers that the arsenic present in superphosphates may sometimes explain the bad effects occasionally observed. Arsenic acid is injurious to germination, and arsenious acid is much more injurious than arsenic acid. The author's experiments gave discordant results. In some cases arsenic acid was favourable to germination, but this is attributed to its destructive action on the microbes present on the surface of the seeds. N. H. J. M.

Mean Molecular Weight of the Soluble Matter in Germinating Grain. By LÉON MAQUENNE (*Compt. rend.*, 1897, 125, 576—579).—The grain was allowed to germinate in presence of distilled water for a definite time, and was then crushed and pressed, the freezing point of the liquid and the quantity of dissolved solid matter in it being determined either with or without previous dilution with water as the case might require. From the data thus obtained, the mean molecular weight of the dissolved matter was calculated. In the case of rye, after germinating eight days, it was 445; after twelve days, 203; and after thirty days, 167: in the case of peas, after eight days, 306; after fifteen days, 199, and after forty days, 112: in the case of white lupin, after fifteen days, 239; after twenty-two days, 226; and after forty days, 137. Although the molecular weights differ widely in the case of different plants, it is clear that, for the same species, the mean molecular weight of the soluble matters diminishes as germination proceeds. It would follow that the transformation of the reserve matter in the seed does not consist, as is generally supposed, simply of a conversion of amylaceous substances into sugars, and of proteids into simple amides. Glucose and asparagine are probably the ultimate terms of the transformation, but their formation is preceded by that of soluble intermediate products. In the cases of peas and lupins, for example, no glucose can be detected in the soluble products after eight days germination.

Similar determinations of the mean molecular weight of dissolved substances in the juice of different parts of green wheat soon after flowering gave the following results. Near the root, 176; middle of plant, 194; near the ear, 215. The molecular weight of the soluble

matter therefore increases as it ascends the plant, and gradually approaches the point where it will ultimately be stored up in the seed, Experiments showed that the osmotic pressure was practically the same in all parts of the plant.

C. H. B.

Substitution of Arsenic Acid for Phosphoric Acid in the Nutrition of Plants. By JULIUS STOKLASA (*Ann. Agron.*, 1897, 23, 471—477).—Oats were grown in nutritive solutions (1), without phosphorus or arsenic, (2), with phosphoric acid (0·00142 per cent.) and arsenic acid (as sodium salt, 0·0023 per cent.), (3), with phosphoric acid (0·0142 per cent.), and (4), with arsenic acid (0·0023 per cent.) but without phosphoric acid. The following results were obtained :

	Average length		Dry produce			Number of seeds.	Lecithin in leaves. per cent.	Furfuraldehyde in leaves. per cent.
	roots. cm.	stems. cm.	roots. grams.	stems, &c. grams.	seeds. grams.			
1.	9·3	36·2	0·63	2·96	—	—	0·38	8·11
2.	33·2	95·4	4·6	13·65	6·85	347	1·46	8·43
3.	35·6	96·7	4·8	14·38	7·32	368	1·35	8·09
4.	18·5	49·3	1·02	4·84	—	—	0·41	10·27

The plants of series 4 (with arsenic) developed better than those of series 1, but the flowers soon dried up and the leaves were bluish-green. In presence of phosphoric acid, arsenic acid had no injurious effect.

It was previously shown that chlorophyll formation (and consequently assimilation of carbon) depends on the presence of lecithin, a compound containing phosphorus, produced by the interaction of glycerophosphoric acid, choline, and chlorophyllanic acid. In these experiments, the leaves produced under the influence of arsenic acid contained only about the same amount of lecithin as in series 1. On further examining the leaves, it was found that those of series 1, 2, and 3 contained chlorophyll grains, often accompanied with starch, whilst those of series 4 contained chlorophyll grains but no starch. In absence of phosphorus and arsenic, the leaves were yellow. Furfuroids were produced in largest quantity under the influence of arsenic acid alone (they were determined as furfuraldehyde. See table). In favouring the formation of furfuroids, arsenic acid increases the development of assimilating organs.

Whilst 0·02 per cent. of arsenic acid is injurious to vegetation, as little as 0·0002 per cent. of arsenious acid is sufficient to destroy plants.

N. H. J. M.

Transformation of Sugars into Oil in the Olive. By C. GERBER (*Compt. rend.*, 1897, 125, 658—661).—The respiratory quotient CO_2/O_2 for olives is less than unity when they are young, and when, as Luca has shown (*Compt. rend.*, 1861 and 1862), they contain a high proportion of mannitol and a very low proportion of oil. It becomes greater than unity when they are large and when they change to violet-red, and at this period Luca found that the proportion of mannitol diminishes, whilst that of oil increases. Since the olives contain neither citric, tartaric, nor malic acid, and no alcoholic fermentation

goes on in the fruit, it follows that the excess of the respiration quotient above unity indicates that the oil is being formed at the expense of the mannitol.

C. H. B.

Quantity of Pentosans and other Carbohydrates in Peat. By H. VON FEILITZEN and BERNHARD TOLLENS (*Ber.*, 1897, 30, 2571—2576).—The formation of furfuraldehyde from vegetable matter on distillation with hydrochloric acid cannot be taken as a certain indication of the presence of pentosans, since other substances such as glycuronic acid, &c., yield it under the same conditions.

The quantity of pentosans present in the peat was determined by the Krüger-Tollens method, the largest quantity being found in the upper layers, and decreasing with the depth, the amount being roughly inversely proportional to the carbon present. The quantity of cellulose also decreases with the depth, the amount present in a sample of *Sphagnum cuspidatum* at the surface being 21.11 per cent., at 20—100 cm. deep, — 15.20 per cent., and at 100—200 cm. deep, — 6.87 per cent.

On hydrolysing the peat, mannose, galactose, levulose, and pentoses were detected in the product.

J. F. T.

Fermentation of Peat. By H. VON FEILITZEN and BERNHARD TOLLENS (*Ber.*, 1897, 30, 2577—2581).—Experiments were carried out with the object of obtaining alcohol from peat by hydrolysing with sulphuric acid and fermenting the glucoses thus formed with yeast. The following table shows the results obtained.

	Sugar before fermentation.	Pentoses.	Fermentable.	Alcohol theory.	Alcohol found.
Speekener Moor I. (20—100 cm.).....	27.87	14.49	13.38	6.84	6.79
II. (100—200 cm.) ...	22.71	11.08	11.63	5.94	5.46
III. (200—300 cm.) ...	11.22	6.67	4.55	2.33	1.48

The upper, least decomposed, peat layers yield, therefore, more alcohol than the lower dark coloured layers rich in carbon.

J. F. T.

Composition of Oats. By BALLAND (*Compt. rend.*, 1897, 125, 579—581. Compare Abstr., 1896, ii, 64).—There is no relation between the mean weight of the grains, the weight of grains per hectolitre, and the colour of the oats, nor between these factors and the proportion of cellulose, fat, and inorganic matter in the oats. As a rule, however, in the case of Russian oats, the white contain a higher proportion of nitrogen than the black. There are also no definite relations between the weights of the ash (inorganic matter), cellulose, fat, and nitrogen, except that in the same species a maximum of cellulose always coincides with a reduced proportion of nitrogen. There are no general relations between the weight of the kernel or of the husk and the mean weight of the grains or the weight of grain per hectolitre; white oats often give less kernel than black oats, but the contrary is the case with Russian oats. The ratio of kernel to husk varies greatly in different localities; in hot climates, the proportion of husk is always high, although its composition is the same as in temperate climates, whereas the proportion of nitrogen in the kernel is much higher in hot climates than in temperate. Algerian oats contain as much or more nitrogen than the best oats from some European

localities, although they contain a considerably higher proportion of husk. For oats of the same species, the nutritive value increases with the weight of the kernel. The composition of an alcoholic extract of oats varies greatly with the concentration of the alcohol; with absolute alcohol, fats only and no nitrogenous matters are dissolved, but with more and more dilute alcohol the proportion of nitrogenous matter dissolved increases. No alkaloid is present, and the irritant properties observed by Sanson (*Abstr.*, 1884, 914) are probably due to an essential oil present in small proportion. The high proportion of fat in oats, combined with the proportion of nitrogenous matter and phosphates, makes them a more complete food for men and animals than either wheat, barley, or rye.

Whole oats can be kept for several years without any appreciable change in their composition, but when they are crushed changes take place, the acidity rises rapidly, and the fats undergo alteration. The composition of oats varies greatly according to latitude and climate; even with the same species in the same district the composition varies with the season. Analyses of a thousand varieties of oats grown or imported into France in the years 1893—1897 show that the variations are of the following order:—Water, 9·80 to 17·00; nitrogenous matter, 7·10 to 14·13; fats, 2·89 to 6·82; sugars and starches, 56·95 to 64·32; cellulose, 7·02 to 12·24; ash, 1·88 to 6·90 per cent. Weight of the kernel, 61·00 to 79·50; and weight of the husk, 20·50 to 39·00 per cent. Mean weight of 100 grains, 1·80 to 4·32 grams. C. H. B.

Composition of the Seeds and Etiolated Seedlings of *Lupinus angustifolius*, L. By M. MERLIS (*Landw. Versuchs-Stat.*, 1897, 48, 419—454).—The following summary shows the amounts of the different constituents, (1), in 100 parts of the dry seeds freed from husks; (2) in the corresponding amount (72·212 parts) of dry etiolated plants, 15 days old; and (3) the loss or gain.

	N.	Proteids.	Nuclein, &c.	Lupeose.	Glyce- rides.	Lecithin.	Choles- terol.	Cellu- lose.	Insol- N-free extract.	Aspara- gine.
1.	6·61	36·18	0·88	11·34	7·48	2·20	0·20	1·58	27·89	0
2.	6·56	7·63	1·53	0	1·62	1·14	0·46	8·44	11·77	18·17
3.	-0·05	-28·55	+0·65	-11·34	-5·86	-1·06	+0·26	+6·86	-16·12	+18·17

Under nuclein, &c., indigestible nitrogenous substances are included, and under glycerides, free fatty acids. The amounts of ash were, (1) 3·51, (2) 3·83, and (3) +0·32 parts. The seeds contained, besides the above, 0·31 per cent. of alkaloids.

The etiolated seedlings were found to contain leucine, amidovaleric acid, and choline. Arginine was not present unless in traces. Phenyl- α -amidopropionic acid was probably present in very small amounts.

The results show, in the first place, that the total nitrogen of the seeds and of the seedlings is practically the same, and that germination is not accompanied with loss of nitrogen. The proteids break up, yielding asparagine, amido-acids, and bases. The carbohydrates of the seeds diminished considerably, the lupeose (β -galactan) disappearing completely after 8—9 days, whilst there was a great increase of cellulose. The increase in ash may be due to the action of water on the

glass, or to the production of sulphates in the breaking up of the proteids.

In order to ascertain to what extent the constituents of the cotyledons are utilised during the development of seedlings, the amounts of the different seeds freed from husks were compared with the amounts in the cotyledons of seedlings $2\frac{1}{2}$ weeks old. The following are the amounts (in grams) in (1) 1000 seeds (dry matter = 102.0 grams), and (2) 2000 cotyledons (dry matter = 21.59 grams).

	N.	Proteids.	Crude fat.	Lecithin.	Cellulose.	Insol. N-free extract.	Ash.
1.	6.64	37.14	7.04	2.26	1.77	28.17	3.36
2.	1.67	1.92	0.94	0.25	2.01	3.54	1.19

The results show that the reserve proteids, the fat and lecithin, are almost entirely consumed in $2\frac{1}{2}$ weeks, whilst most of the nitrogen-free extract also disappeared.

With regard to the decomposition of proteids during the growth of etiolated seedlings, the nitrogen in different forms was determined at intervals of three days. The following results show the amounts in 100 parts of dry seeds and in the corresponding amounts of seedlings at the different dates.

	Dry matter.	Nitrogen.			
		As proteids.	As as- paragine.	Inphosphotungstic acid precipitate.	In difference.
Seeds	100	6.14	—	0.42	—
Seedlings, 3 days	96.08	5.56	0.49	0.45	0.11
„ 6 „	89.20	3.19	1.93	0.49	1.00
„ 9 „	82.73	2.38	3.19	—	—
„ 12 „	75.80	1.93	3.75	—	—
„ 15 „	72.72	1.49	3.85	0.45	0.82
„ 18 „	70.69	1.51	4.23	0.43	0.34

The rapid decomposition of proteids in the early period of growth is in accordance with the observations of Prianischnikoff (Abstr., 1895, ii, 124; compare E. Schulze, *Vierteljahrschr. naturforsch. Ges. Zürich*, 1894, 264). The increase of asparagine in the last period, when there was no corresponding decrease of proteids, would seem to indicate a transformation into asparagine of other products of the decomposition of proteids. This would lend support to the view that asparagine is not a primary product from proteids. N. H. J. M.

Losses and Chemical Changes in Vegetable Foods when kept for a long time at High Temperatures. By HUGO WEISKE (*Landw. Versuchs-Stat.*, 1897, 48, 379—389).—A number of glass jars were filled with hay and heated in a water oven. Half of the jars were left open, whilst the other half were closed after moistening the contents with distilled water. The hay was analysed in its original condition, and at intervals of a month, for 6 months. The dry hay gradually became light brown, whilst the moistened hay soon acquired a dark brown colour. There was a progressive loss of dry substance in both cases, but much more with the damp than with the dry hay. The amounts of ether extract and of crude fibre diminished, whilst the proteids, and especially the non-nitrogenous extract, increased.

There was, however, a very great decrease of digestible proteids; whilst the original hay contained 1·21 per cent. of digestible, and 0·76 per cent. of indigestible, nitrogen, the dry hay contained, after 6 months heating, digestible, 0·46; indigestible 1·72 per cent., and the damp hay, digestible 0·25, indigestible 2·04 per cent. Heating for 4 days had practically no effect on the digestibility of the proteids.

N. H. J. M.

Action of Potassium Chloride on the Lime Resources of the Soil. By CHARLES A. GOESSMANN (*Hatch Exper. Stat. Mass. Agric. Coll. Bull.*, 38, 1896, 14—16).—Experimental plots which had for years received potassium chloride yielded crops of unhealthy appearance. After an application of slaked lime (500—600 lbs. per acre), the succeeding crop was healthy. Analyses of the drainage from each plot at the end of the season, showed the presence of a larger amount of lime in the case of plots which had received potash in the form of chloride, than where potassium sulphate had been applied.

It is concluded that when land containing limited amounts of lime is manured with potassium chloride, lime should be directly applied from time to time. It is safer to apply potassium chloride to deep soil with a free subsoil, than to a shallow soil with a compact clay subsoil. In the latter case, there is a possibility of an excessive accumulation of calcium and magnesium chlorides near the roots of the plants.

N. H. J. M.

Remarkable Observation on Ignited Basic Slag By MAX SCHMOEGER (*Landw. Versuchs-Stat.*, 1897, 48, 413—418).—Basic slag (5 grams) was fused with precipitated silica (0·6 gram) and the phosphoric acid determined in the product, as well as in the original slag, and in the slag fused without silica. The following results were obtained :—

	SiO ₂ .	P ₂ O ₅ .	
	per cent.	Total per cent.	Citrate-soluble per cent. of total.
Original slag.....	2·23	20·19	48·4
Fused with silica	12·07	17·80	83·5
Fused without silica	2·25	19·87	20·1

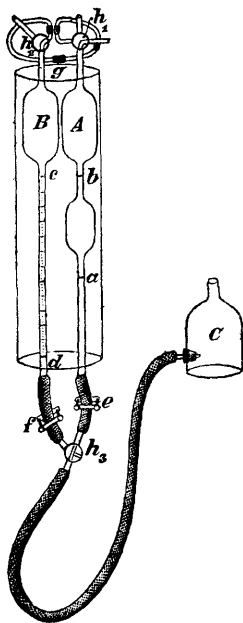
The fused samples were ground more finely than the original slag before analysis. Whilst fusion without silica resulted in a gain in weight (0·5 per cent.), when fused with silica the substance lost about 0·6 per cent. in weight owing to evolution of carbonic anhydride.

Two other samples of slag were ignited with and without silica. With silica, there was, as before, an increase in soluble phosphoric acid. Without silica, there was also a distinct increase, instead of a decrease, in soluble phosphoric acid, and there was a decrease instead of an increase in weight. (Compare G. Hoyer mann, *Die Citratlöslichkeit d. Phosphorsäure in Thomasmehl.*)

N. H. J. M.

Analytical Chemistry.

Four New Methods of Measuring Gases. By OTTO BLEIER (*Ber.*, 1897, 30, 2753—2759).—A new compensation method is first described, in which it is not the standard gas, but the gas under examination, that is kept constant in volume, or is adjusted to a known fraction of its original volume. The apparatus in the figure, which is designed for the analysis of ordinary air, is surrounded by a water-jacket. A is filled with the gas to be examined and holds 100 c.c. down to the mark *a*, 79.5 c.c. down to the mark *b*. B contains the standard volume of air; it holds 100 c.c. down to *c*, and the space



between *c* and *d* contains 1 c.c. and is graduated in 0.01 c.c. Both vessels having been filled, to *a* and *c* respectively, at the atmospheric pressure, their upper extremities are connected by means of the capillary tube shown in the figure; there is a drop of liquid in the centre of this, which drop will remain in the centre if the two stop-cocks (*h*₁ and *h*₂) be opened. After absorption of the carbonic anhydride, the liquid is brought to its original levels (*a* and *c*) in A and B, and the two stop-cocks are opened. There is now a slightly diminished pressure in A, owing to the absorption that has taken place, and consequently the drop of liquid moves towards A; the liquid in *c*, *d* is lowered until the drop comes back to its original position. If the volume from *c* to the point to which it has been lowered is 0.15 c.c., then the percentage of

carbonic anhydride is $0.15 \times \frac{100}{100.15}$. The oxy-

gen is now absorbed, and the same process is again gone through, except that the liquid in A is brought to the level *b* instead of *a* (*ab* = 20.5 c.c.). Supposing the final level in *cd* to be 0.53 c.c., then the percentage of

oxygen is $20.5 + 0.53 \times \frac{100}{100.53}$. The advantage of this method is that

the measurements are made with great accuracy, and, further, all under approximately the same pressure, so that the use of water is permissible. A special apparatus is required, however, for the analysis of any particular gas, as measurements can only be made in the neighbourhood of those percentages with which the fixed marks on A correspond.

The apparatus figured can also be used for compensation measurements in the ordinary way, the gas under examination being the one of which the volume is accurately measured. This gas is then con-

tained in B which it fills to d , the volume down to this point being now 100 c.c. ; A now contains the standard volume of air, and is filled only to b under atmospheric pressure. After absorption of carbonic anhydride, the percentage absorbed is measured by the rise in d , c , when the drop of liquid has been adjusted to its initial position in the capillary tube. In measuring the oxygen absorbed, the level in A must be brought to a . A combination of the two methods may also be adopted, both pipettes being graduated below ; the second method is used first, as far as the apparatus allows, and then the first method.

An arrangement is next described which permits of measurements of volume by means of pressure readings. The pipette, which is enclosed in a water-jacket, consists of 5 bulbs, each approximately of 20 c.c., on the narrow connecting-tubes of which marks are placed, one between each pair of bulbs ; the volume of the pipette down to each of these marks is accurately known. In connection with this measuring pipette, there is a movable reservoir and a graduated manometer tube which is clamped in position and extends about 60 cm. above and below the lowest mark of the pipette ; at the same levels as this mark and those above it, marks are drawn on the manometer. The gas is first compressed to the lowest mark and the pressure noted in the manometer ; after the absorption of one of the constituents, the pressure is again noted, the volume being adjusted to the same mark, or, if that is impossible, to one above it. This apparatus can be used with water.

Lastly, a measuring pipette with reserve spaces is described. This is enclosed in a water-jacket, and consists of two parallel vertical branches. One branch is a cylindrical tube, graduated, and holding 20 c.c. from the uppermost to the lowermost graduation ; the other consists of 4 bulbs, with marks, one on the constriction below each bulb ; the volume from the uppermost graduation on the other tube to these marks is known accurately, and is approximately 20, 40, 60, and 80 c.c. The two branches are joined in one piece at the top by a connecting tube to which the glass stop-cock for the admission of the gas is also fused ; at their lower ends, the two branches are connected with a movable reservoir, by means of a three-way tube and india-rubber tubing. In measuring the gas, the liquid is first driven up to one of the marks (whichever is suitable), the india-rubber tubing below this is closed by a spring clip, and then the reservoir is adjusted so that the level of the liquid is the same in it as in the graduated branch of the pipette ; the volume of the gas is then read off. C. F. B.

Separation and Estimation of Chlorine and Bromine in a Mixture of Alkali Salts. By HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1897, 125, 607—610).—When estimating bromine by expelling it from solutions of bromides by the combined action of cupric sulphate and potassium permanganate (this vol., ii, 90), the concentration of the liquid is an important factor ; if the solution is dilute, a relatively larger quantity of copper sulphate must be added in order to ensure complete liberation of the bromine. Provided that an excess of permanganate is present, the exact proportion of it has little influence on the accuracy of the result. Direct experiments show that chlorides are not decomposed under the conditions specified, provided

the quantity in 100 c.c. of liquid containing 15 to 16 grams of crystallised copper sulphate and 0.7 to 0.8 gram of potassium permanganate is not equivalent to more than the 0.250 gram of sodium chloride; under these conditions, however, the whole of the bromine is liberated. The time required for complete elimination of the bromine is practically unaffected, within ordinary limits, by the proportion of bromide present, but the last traces of the bromine are somewhat difficult to expel.

C. H. B.

Detection of Traces of Bromine by Means of Fluorescein. By HENRI BAUBIGNY (*Compt. rend.*, 1897, 125, 654—657).—Paper prepared with a somewhat concentrated solution of fluorescein in acetic acid is placed in the mouth of the vessel, or in a tube leading from the vessel from which the gas or vapour supposed to contain bromine is issuing. The presence of even minute quantities of bromine is indicated by the appearance on the paper of pink streaks, due to the formation of eosin. The method is not applicable to mixtures of small quantities of free bromine with large quantities of free chlorine, but in the case of a mixture of chloride and bromide the bromine can be liberated by means of copper sulphate and potassium permanganate.

C. H. B.

Estimation of Phosphorus in Steel, Iron, and Iron Ores. By JULIUS OHLY (*Chem. News*, 1897, 76, 200—201).—Two grams of steel are dissolved by heating with 45 c.c. of nitric acid of sp. gr. = 1.16, 5 c.c. of saturated potassium permanganate solution is added, and the whole boiled until the pink colour disappears; five or six drops of saturated sugar solution is then dropped in to dissolve the precipitate, avoiding excess, and the whole cooled to 60°. It is then shaken with 5 c.c. of ammonia until clear, 30 to 40 c.c. of molybdate solution is added, the whole well shaken, filtered, washed six times, and the flask mixed with 2 per cent. nitric acid, then with 2 per cent. potassium nitrate. The filter and precipitate are returned to the flask, the precipitate dissolved in 25 c.c. of standardised sodium hydroxide, and three or four drops of phenolphthalein added to the solution, which is then titrated with nitric acid, standardised against steel having a known percentage of phosphorus.

The measurement of the bulk of the molybdate precipitate, and so indirectly of the phosphorus, in a Goetz tube is also suggested.

D. A. L.

Estimation of Nitrogen in Guano. By V. SCHENKE (*Chem. Zeit.*, 1897, 21, 490).—The author has proved by a series of analyses that the nitric nitrogen contained in guanos is best calculated from the difference between the total nitrogen and that obtained by Kjeldahl's process.

Haselhoff's water extraction method gives untrustworthy results, although better results may be obtained by using cold water (compare this vol., ii, 36).

L. DE K.

Estimation of Phosphoric Acid as Phosphomolybdic Anhydride. By Woy (*Chem. Zeit.*, 1897, 441—443, 469—472).—The following reagents are required. A solution of 120 grams of ammonium molybdate in 4 litres of water; a solution of 340 grams of

ammonium nitrate in 1 litre of water; nitric acid of 1.153 sp. gr.; a washing solution containing 200 grams of ammonium nitrate and 160 c.c. of the nitric acid (sp. gr. 1.153) in 4 litres.

The sample is dissolved in sulphuric acid, made up to a definite bulk, and an aliquot part, representing about 0.5 gram of material, is neutralised with ammonia and mixed with 10 or 20 c.c. of nitric acid; after adding 30 c.c. of the ammonium nitrate solution, the liquid is heated to boiling, and a slight excess of the molybdate solution is added, 5 c.c. of which is equivalent to about 1 per cent. of phosphoric acid in the sample. The precipitation is complete within 15 minutes, and the deposit is collected and washed with 50 c.c. of the hot washing solution. To purify it, it is dissolved in 10 c.c. of an 8 per cent. solution of ammonia and then mixed with 20 c.c. of the ammonium nitrate, and also 1 c.c. of the molybdate solution. After heating to boiling, 20 c.c. of hot nitric acid is added to reprecipitate the compound. It is then collected in a Gooch's crucible, and after being washed with the acid ammonium nitrate, it is ignited at a dull red heat. The black residue contains exactly 3.946 per cent. of phosphoric anhydride.

L. DE K.

Toxicological Detection of Arsenic. By E. FRICKE (*Chem. Zeit.*, 1897, 21, 303).—When using Marsh's test, it sometimes happens that very slight mirrors are obtained which, however, may consist of carbon. In order to positively say whether arsenic is absent, the author recommends the following process.

The decolorised solution is, as usual, treated with hydrogen sulphide, the precipitate which forms is dissolved in ammonium sulphide, the solution evaporated to dryness and the residue fused with sodium carbonate and nitrate; the melt is then dissolved in water, evaporated with sulphuric acid, and the residue dissolved in water and again treated with hydrogen sulphide. Owing to the complete absence of organic matter, any yellow coloration or precipitate points to the presence of arsenic, but if the liquid remains clear, arsenic is certainly absent. To ascertain whether the yellow precipitate is really arsenic it must be tested in the Marsh's apparatus.

L. DE K.

Detection of Thioxyarsenic Acids. By LE ROY W. McCAY (*Chem. Zeit.*, 1897, 21, 487).—A dilute solution of sodium orthomono-thioxyarsenate gives with strontium chloride a white, amorphous precipitate of the corresponding strontium salt which soon becomes crystalline, whilst if barium chloride is added to the dithioxy-salt of sodium, the corresponding barium salt is produced. In this way, the two arsenical compounds may be separated by first removing the mono-compound with strontium chloride and then precipitating the di-salt by barium chloride.

The mono-compound may also be utilised for separating calcium from barium.

L. DE K.

Titration of Sodium Thiosulphate with Iodic Acid. By CLAUDE F. WALKER (*Amer. J. Sci.*, 1897, 4, 235—242).—Riegler has stated that sodium thiosulphate may be titrated by means of iodic acid, using starch as indicator; directly all the thiosulphate is

converted into tetrathionate and iodide, the addition of more iodic acid liberates iodine and gives rise to a blue coloration. By a long series of experiments, the author has proved that the reaction between iodic acid and sodium thiosulphate is so indefinite in its nature and so influenced by time, dilution, and mass, that the method proposed by Riegler is quite impracticable.

L. DE K.

Estimation of Carbon Bisulphide in Alcohol. Carbon Tetrachloride, &c. Purification of Carbon Tetrachloride and a New Compound of the same. By W. SCHMITZ-DUMONT (*Chem. Zeit.*, 1897, 21, 487—488, 510—511).—The usual process is to boil the spirit with potassium hydroxide dissolved in alcohol, the potassium xanthate thus produced being estimated in various ways. The author prefers oxidising it with potassium permanganate in an alkaline solution, and estimating the sulphuric acid thus produced.*

The results are, however, generally a trifle low; the following method is better: 10 c.c. of the sample is heated with 20 c.c. of alcoholic solution of lead acetate and 10 c.c. of normal alcoholic potash for 20 minutes at 50—60°; the lead sulphide formed is then collected, and the sulphur converted into sulphuric acid by means of nitric acid and bromine. Another process is given, based on the formation of silver sulphide; 10 c.c. of the sample is mixed with 50 c.c. of a 5 per cent. alcoholic solution of silver nitrate and 5 c.c. of aniline, and the whole is then heated for half an hour at 60°; the silver sulphide thus obtained is afterwards fused with sodium nitrate and carbonate, to convert the sulphur into sulphate.

Carbon tetrachloride may be freed from carbon bisulphide by dissolving a quantity of potassium hydroxide, more than sufficient to decompose the carbon bisulphide, in 100 c.c. of alcohol, and adding this to a litre of the chloride. After heating for half an hour at 60°, the xanthate is precipitated by adding water, and the liquid is repeatedly washed with water until free from alcohol. To free the tetrachloride from any trichloride, it is first dried over potassium hydroxide and then distilled over paraffin.

The author has found that, on prolonged contact, carbon tetrachloride and phenylhydrazine yield silky needles of the composition $(C_6H_5 \cdot NH \cdot NH_2)_2HCl$.

L. DE K.

[* NOTE BY ABTRACTOR.—In reference to the oxidation of sulphur in an alkaline solution by means of permanganate, compare Abstr., 1895, ii, 184.]

Cyanide Titration of Copper. By HARRY BREARLEY (*Chem. News*, 1897, 76, 189—191).—To avoid the uncertainty connected with the ordinary method in which the discharge of colour is taken as the final stage, the author suggests running in cyanide until this stage is reached, then adding potassium iodide and titrating back to a permanent turbidity with silver nitrate. He finds in this case also (compare Davies, *Chem. News*, 1888, 58, 131) that the use of sodium carbonate instead of ammonia is advantageous, inasmuch as increasing volume of liquid or quantity of alkali, or copper, or cyanide, or the presence of alkali chlorides, nitrate, or acetates seriously derange the titration in the latter, but not in the former case (compare Thomson.

Chem. News, 1880, 33, 152, and J. J. and C. Beringer, *Abstr.*, 1884, 113), except with nitrates, and this can be overcome by using greater excess of sodium carbonate; nitrates, acetates, and sulphates, however, but not chlorides, cause a more or less inky solution that masks the turbidity due to the silver iodide, but the addition of sodium chloride cures this defect. In the presence of ferric iron, the usual method is useless, the modified method successful, whilst in the presence of aluminium or manganese the results accord with the usual titration. Besides manganese, nickel, cobalt, zinc, mercury, silver, gold, platinum, and palladium interfere with the reaction. D. A. L.

Estimation of Mercuric Salts. By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1897, 30, 2808—2809. Compare *Abstr.*, 1897, ii, 601).—The solution is mixed with excess of commercial hydrogen peroxide (containing hydrochloric acid), phosphorous acid is added, and the whole is warmed on the water bath until the precipitate of mercurous chloride has clotted; this precipitate is collected on a tared filter, dried at 105°, and weighed. In five experiments, the percentage of Hg found was 73·82—74·01; calculated 73·85. Phosphorous acid may thus be used as a reducing agent, instead of hypophosphorous acid; the hydrogen peroxide prevents a further reduction to metallic mercury, which otherwise would take place at the temperature of the water bath.

C. F. B.

Analysis of White Paints. By GUSTAVE W. THOMPSON (*J. Soc. Chem. Ind.*, 1896, 15, 432—434, 791).—The pigments most frequently met with in the white paints of commerce are white lead, lead sulphate, zinc oxide, the so-called “sublimed white lead,” which consists of lead sulphate with varying proportions of lead and zinc oxides, barytes, calcium sulphate, calcium carbonate, china clay, silica, zinc sulphide, and lead sulphite. For extracting the oil, the author prefers “C. P. benzol” although any of the usual solvents may be used; sufficient organic matter may remain, however, to render valueless any direct estimation of combined water. The exact course of the quantitative analysis will depend on the results of a previous qualitative examination, in which the solubility of all lead compounds (except sulphite), zinc oxide, and calcium salts in boiling acid ammonium acetate is mainly to be depended on. The methods recommended for the estimations are in the main those of the ordinary text-books; only the special methods are, therefore, noticed here. White lead is calculated according to circumstances either from a carbonic anhydride estimation, or from the lead soluble in acetic acid, the arbitrary formula, $2\text{PbCO}_3, \text{PbH}_2\text{O}_2$, being adopted. For the separation of lead compounds (other than sulphite) from barytes, china clay, &c., their solubility in acid ammonium acetate is made use of. Lead sulphate may be regarded as insoluble in acetic acid, and be thus separated from lead oxide and white lead. Since a mixture of lead sulphate and calcium carbonate cannot be treated with water without the occurrence of double decomposition, calcium sulphate cannot be dissolved out from a mixture of the three substances. The total calcium must be estimated in one portion, and another portion be treated with a cold mixture of 9 parts of 95 per cent. alcohol and 1 part of nitric acid (sp. gr. = 1·4), which dissolves the calcium car-

bonate and leaves the calcium sulphate. A gram of the sample is treated four times with this solvent, for 20 minutes each time, and the decanted and filtered liquids are evaporated to dryness. The residue is heated with excess of strong sulphuric acid until fumes appear, then dissolved in acidified ammonium acetate, freed from lead and zinc by hydrogen sulphide, and the calcium estimated as usual. M. J. S.

Separation of Aluminium from Beryllium by the Action of Hydrochloric Acid. By FRANK S. HAVENS (*Amer. J. Sci.*, 1897, [iv], 111—114, and *Zeit. anorg. Ch.*, 16, 15—18).—The author, in a previous communication (Abstr., 1897, ii, 232), has proved that alumina may be completely separated from iron oxide by dissolving in hydrochloric acid, adding an equal bulk of ether, and saturating it with hydrogen chloride. The aluminium is then completely precipitated as chloride, which, after being washed with a mixture of acid and ether saturated with hydrogen chloride at 15°, is converted into oxide by ignition with mercuric oxide.

The author now states that the process is equally applicable in the presence of beryllium. After removing the aluminium as described, the filtrate is evaporated to dryness and the residue is converted into nitrate by evaporating with nitric acid. This, on strong ignition, leaves pure beryllium oxide.

The test analyses show the great accuracy of the process.

L. DE K.

Assay of Carbonated Manganiferous Minerals. By N. DEVISSE (*Chem. News*, 1897, 76, 212—213).—Manganese, when precipitated in the presence of oxidising agents, tends to form compounds of the general formula $5\text{MnO}_2, \text{MO}$; MO being manganous, zinc, calcium or other oxide: for example, by adding 1 equivalent of permanganate to four equivalents of manganous chloride, neutralising the liberated acid, all the manganese is precipitated in this form, as shown in the equation $4\text{MnCl}_2 + \text{Mn}_2\text{O}_8\text{K}_2 + 3\text{H}_2\text{O} = 5\text{MnO}_2, \text{MnO} + 2\text{KCl} + 6\text{HCl}$. The presence of zinc or lime salts might in this way affect gravimetric results, hence volumetric methods are advocated, and if precipitated zinc oxide is added prior to the treatment with permanganate in Volhard's method, then the chlorides need not be transformed into sulphates.

D. A. L.

Estimation of Iron and Aluminium in Mineral Phosphates, Manures, Alum, &c. By ROBERT T. THOMSON (*J. Soc. Chem. Ind.*, 1896, 15, 868—869).—In an earlier paper on this subject (Abstr., 1887, 302), the precipitation of iron and aluminium phosphates, free from calcium, from a solution containing calcium phosphate, was effected by ammonium acetate strongly acidified with acetic acid. Gladding (Abstr., 1897, ii, 125) adopts the same method, with the condition that the solution be heated to 60°, but in either case several reprecipitations may be necessary to ensure complete absence of calcium from the precipitate. This difficulty appears to be a direct result of the presence of ammonium acetate, and the author, therefore, now reverts to his "neutralisation" method, which consists in the cautious addition of ammonia to the hydrochloric acid solution of the mixed phosphates, until sensitive blue lacmoid paper indicates that only a

minute trace of free acid remains. One part of aluminium phosphate requires 3 parts, and 1 part of ferric phosphate 12 parts of free phosphoric acid to hold it in solution, so that with care in the neutralisation the precipitation of both is practically perfect, whilst the precipitate is completely free from calcium. The aluminium and iron phosphates so precipitated will be normal phosphates if the solution contained at least 1.5 times the theoretical proportion of phosphoric acid, otherwise they will be basic. This normal composition, and also the gelatinous condition, will be retained if the precipitate is washed with a 1 per cent. solution of ammonium nitrate containing 0.2 gram of ammonium dihydrogen phosphate per litre, this solution being, if necessary, carefully made neutral to methyl-orange by the addition of phosphoric acid. Although the portion of this solution retained by the drained precipitate will leave its phosphoric acid when the precipitate is ignited, the error is too small to be of importance. Should the substance under analysis contain calcium fluoride, the evaporation of its hydrochloric acid solution to dryness with nitric acid will eliminate the fluorine. The nitric acid should not be added until the hydrochloric acid solution has been filtered from any pyrites which the substance may contain, because this mineral is left unaffected in the manufacture of superphosphate, and its iron should, therefore, be reported separately.

The above process serves equally well for the separation of aluminium and iron from nickel, cobalt, zinc, manganese, and magnesium.

M. J. S.

Separations with Alkali Acetates. IV. Chromium from Iron. V. Aluminium and Copper from Iron. VI. Zinc from Iron. By HARRY BREARLEY (*Chem. News*, 1897, 76, 175—177, 210—211, 222—224. Compare Abstr., 1897, ii, 388, and this vol., ii, 96).—*Chromium* cannot be separated quantitatively from iron by means of sodium acetate either when much or little acetate or free acid is used, although the separation is better when the larger quantities are employed, especially with plenty of strong acetate. The separation, too, is better in the case of a chrome steel containing from several tenths to 2 or 3 per cent. of chromium than it is from solutions having 0.1 gram of chromium to 1 gram of iron. The imperfect separation is attributed to the formation of iron chromates, and it seems that aluminium forms similar compounds with iron, since no useful separation of *aluminium from iron* can be effected by alkali acetates, whether in the presence of much, little, or no acetic acid, or dissolved hydroxide. A much larger quantity of acetate is required to completely precipitate the iron in the presence of much aluminium, some of which is also precipitated. These factors might interfere with some of the separations, but in the case of steel there is usually a harmless amount of aluminium and as much as 60 c.c. of acetate and 10 per cent. of aluminium does not greatly upset the nickel and iron separation when 0.1 gram of nickel is present, but under such circumstances this separation would be rendered more perfect by using large amounts of ammonium chloride and less acetate; the use of alkali chromate is likewise mooted for this purpose.

The separation of *copper from iron* by acetate is not quantitative, the presence of free acid, however, favours accuracy, although much acetate has the contrary effect, whilst Schwarzenberg's method is effective for this separation. To estimate copper in steel or iron compounds containing less than 0.5 per cent., the procedure when using sodium cyanide titration is as follows: 5 to 10 grams is dissolved in dilute sulphuric acid, the solution treated with hydrogen sulphide or preferably, with sodium thiosulphate, but only in slight excess, and the liquor poured off through a filter. The precipitate is washed by decantation, and after being mixed with the residue from the ignition of the filter paper, is heated with 10 to 20 c.c. of nitro-hydrochloric acid and potassium chlorate; when all but sulphur is dissolved, the solution is cooled, diluted, neutralised, made alkaline with sodium carbonate, and titrated with sodium cyanide, as described by the author (this vol., ii, 140).

The separation of *zinc from iron* can also be completely effected by the acetate method.

In all the separations by this method, it is to be remembered that the phosphoric acid is precipitated with the iron acetate; that the temperature at which the turbidity appears should be recorded; that cooling the solution before adding the acetate is only necessary when any large excess of acetate is used; that the decomposition of acetates on heating accounts for the presence of free acetic acid in the case of ferric acetate, and may account for some of the imperfect separations recorded by the author; that, knowing the amount of acid used for dissolving, the necessary quantity of alkali required for neutralising may be added at once and the rest several c.c. at a time until there is an unmistakably permanent turbidity, which turbidity is dissipated by adding 10 or 12 c.c. of acetic acid, but, on diluting with hot water and heating, should reappear at about 90°, otherwise a few c.c. of dilute acetate should be added; in this way, nickel in a nickel steel may be determined with great rapidity.

D. A. L.

Estimation of Nickel and Zinc as Phosphate. By JOHN CLARK (*J. Soc. Chem. Ind.*, 1896, 15, 866—868).—Experience has confirmed the value of the ammonio-phosphate process devised by Dirvell and modified by the author (Abstr., 1880, 287; 1884, 498; 1890, 1470) for the separation of cobalt from nickel, but the estimation of the nickel in the filtrate is less satisfactory. By adding dilute hydrochloric acid to the cold or moderately warm liquid until it is neutral or nearly neutral to test-paper, the nickel is precipitated as the double phosphate of the formula $\text{NiNH}_4\text{PO}_4 + 6\text{H}_2\text{O}$; this loses rather more than $5\text{H}_2\text{O}$ at 100°, and on ignition is converted into nickel pyrophosphate. It is slightly soluble in water, but if 20 per cent. of alcohol is added after neutralisation, and the precipitate is washed with cold water containing 10 per cent. of alcohol, the loss is unimportant. If the above process is applied to a mixture of cobalt and nickel salts in which the cobalt exists in the cobaltic state, the nickel only is precipitated. For this purpose, the solution containing the metals as chlorides is mixed with 10 times as much ammonium phosphate as the weight of metal present, and is heated for a few minutes with hydrochloric acid and a considerable excess of bromine. While free bromine is still present,

the solution is supersaturated with ammonia and heated with hydrogen peroxide ; it is then cooled, neutralised with dilute hydrochloric acid as above, and stirred. Alcohol is added, and after several hours the precipitate is collected and washed as above. When much cobalt is present, it may be desirable to re-dissolve in hydrochloric acid, add ammonium phosphate, oxidise, and reprecipitate as before. In this way, 1 part of cobalt may be detected and estimated even when accompanied by 200 parts of nickel.

The above method applied to an ammoniacal solution of zinc chloride, containing enough ammonium chloride to form a double salt, precipitates the whole of the zinc as ZnNH_4PO_4 . This can be washed with cold water, is anhydrous after drying over sulphuric acid, but bears ignition (apart from the filter) without loss of zinc. To apply this method to zinc ores, the iron, alumina, and manganese are removed by ammoniacal hydrogen peroxide, and most of the calcium by ammonium carbonate added to the hot alkaline liquid. The rest of the calcium and the magnesium are thrown down when the ammonium phosphate is added, but this precipitate is free from zinc.

M. J. S.

Assay of Chrome Ore. By ELWYN WALLER (*J. Soc. Chem. Ind.*, 1896, 15, 436—437).—The author reports his experience of the fusion of chrome ore with sodium peroxide in nickel crucibles (see *Trans.*, 1893, 1079, and this vol., ii, 94). About 0.5 gram of ore in impalpable powder was weighed into a nickel crucible (35 mm. in diameter at the top, 30 mm. deep, and weighing 9—12 grams) and well mixed with about 2 grams of dry powdered sodium peroxide. The mass was fused by a small flame and after being kept in tranquil fusion for 8—10 minutes, the temperature was raised to a visible red heat, the crucible being moved for 1 minute in such a way as to give a rotatory motion to its contents. The cooled melt was dissolved in boiling water (50—80 c.c.), the solution boiled for 5 minutes to decompose excess of peroxide, some of which was always found to be present, then filtered, acidified with sulphuric acid, and after dilution to 600—700 c.c. titrated with standard thiosulphate (30 grams per litre), with the addition of potassium iodide (1.5—2 grams) and starch towards the end. Decomposition of the ore was complete ; a single experiment with ore ground only until it would pass through a “60-mesh” sieve indicated that the method would probably serve for such coarse ore. Employment of a shallow basin instead of the crucible resulted in imperfect decomposition. The crucible lost 0.02—0.05 gram at each fusion. The use of a larger proportion of peroxide or a higher temperature caused a stronger attack of the crucible. Heavier crucibles than the above lost proportionally more.

M. J. S.

Estimation of Antimony in Ores and Metals. By JOHN CLARK (*J. Soc. Chem. Ind.*, 1896, 15, 255—257).—If antimony or an antimony ore is dissolved in hydrochloric acid with the assistance of iodine, the oxidation does not proceed beyond the stage of trichloride, and after boiling off the excess of iodine, the solution is at once fit for titration by Mohr's method, using iodine solution in presence of an excess of alkali tartrate and sodium hydrogen carbonate. Should it be found

on adding starch (after the boiling and cooling) that a trace of free iodine remains, this can be cautiously removed by adding sodium sulphite. Since, in acid solution, tin is oxidised to stannic chloride by iodine, it has no effect on the result. Lead is also inert, but in the presence of copper the results are too low; in this case, as also in presence of iron, it becomes necessary to precipitate the metals as sulphides and dissolve out the antimony sulphide by potassium hydroxide. The reprecipitated antimony sulphide is then dissolved by hydrochloric acid and iodine. Arsenic would also vitiate the results, but it can be removed by repeatedly boiling down with copious additions of strong hydrochloric acid.

M. J. S.

Assay of Electro-plating and Gilding Solutions. By ALFRED H. ALLEN (*Chem. News*, 1897, 76, 199).—Whilst approving Baker's method (this vol., ii, 93), the author prefers one he has long used, in which 20—50 c.c. of the plating solution, largely diluted with water and heated to boiling, is treated with hydrogen or ammonium sulphide, and the washed precipitate mixed with excess of bromine water, any sulphur in the residue being oxidised by the use of a small quantity of bromine. Boiling water is then added and the silver bromide washed, dried, fused, and weighed. Electro-gilding or silvering solutions are evaporated in a porcelain crucible to a syrupy consistency, and mixed with red lead or litharge; the mass dried, heated a short time at moderate redness, and the button cupelled, or, in the case of gold, treated with nitric acid, if preferred.

D. A. L.

Preparation of Water Free from Ammonia. By JOSEPH BARNES (*J. Soc. Chem. Ind.*, 1896, 15, 254—255).—Distilled water can be completely freed from ammonia by adding a little bromine and boiling for a few minutes. More rapid is the action of alkaline hypobromite in the cold. Enough bromine is added to the water to give it a perceptible tint, and then a drop of sodium hydroxide solution; after ten minutes, a little potassium iodide is added to remove the undecomposed hypobromite, and the water is then fit for use in the estimation of ammonia by Nessler's test.

M. J. S.

Simplified Organic Analysis (Supplementary Observation). By MAXIMILIANO DENNSTEDT (*Ber.*, 1897, 30, 2861—2962. Compare *Abstr.*, 1897, ii, 432).—In analysing compounds containing nitrogen and halogen by the author's method, the percentage of halogens is often found too high, because the silver retains oxides of nitrogen. After the silver boat has been weighed once, it should be heated in a Bunsen flame till the silver haloids melt, and reweighed, any silver nitrate or nitrite is thus destroyed. It is well to do this in all cases, even when the substance analysed contains no nitrogen.

C. F. B.

Formaldehyde as a Reagent. By HERMANN ENDEMANN (*J. Soc. Chem. Ind.*, 1896, 15, 791—792).—Substances of the phenol class combine with formaldehyde, forming colourless compounds which become coloured on treatment with concentrated sulphuric acid. To obtain the reaction, the phenol is dissolved in commercial formalin, the solution evaporated nearly to dryness at a low temperature, and

concentrated sulphuric acid added. The following reactions have been recorded.

	The solid.	The solution.
Phenol	Magenta-coloured	Magenta-coloured.
Salicylic acid	Red	Magenta.
Eugenol	Brown, with claret shade.....	—
Carvacrol	Orange to orange-red	—
Guaiacol	Violet, quickly brownish-violet	—
Resorcinol ...	Scarlet-red	Orange.
Quinol	Brown	Brown.
Thymol	Faintly fawn-coloured (due to impurity ?)	—
α -Naphthol	Green	Brown.
β -Naphthol	Green, then black	Green.
Pyrogallol ...	Red	—
Hæmatein ...	Red, then brown	—
Tannin	No reaction.....	—

Other aldehydes afford similar reactions, but the colours are different. Silk which has been treated with formaldehyde to render the sericin insoluble gives a different reaction with sulphuric acid (rich brown, passing through olive-green to green as moisture is absorbed) from that of silk not so treated. Washing the treated silk with hot water prevents the colour reaction from being obtained. M. J. S.

Fehling's Solution. By J. E. GEROCK (*Ber.*, 1897, 30, 2865—2867).—The author has tested Siegfried's statement (quoted by Jovitschitsch, this vol., ii, 98) that Fehling's solution undergoes a spontaneous reduction when alkaline sulphates, chlorides, or nitrates are dissolved in it, and found it to be erroneous.

The essential constituent of a Fehling's solution is a compound of the type $R \cdot O \cdot Cu \cdot O \cdot M'$ or $(R \cdot O \cdot Cu \cdot O)_2 M''$, where M' is an alkali, M'' an alkaline earth, and R is an organic radicle not too readily oxidised. The author has used a solution in which the metal was barium and the organic substance salicylic acid. C. F. B.

Reactions of Potassium Ferricyanide with Glucose and their Applications to Volumetric Analysis. By N. TARUGI and G. NICCHIOTTI (*Gazzetta*, 1897, 27, ii, 131—153).—See this vol., i, 118.

Optical Analysis of Urine and Exact Estimation of Proteids, Glucosides, and Non-fermentable Saccharine Materials. By FRÉDÉRIC LANDOLPH (*Compt. rend.*, 1896, 123, 1301—1302).—Small amounts of sugar are best estimated by fermentation. When the sugar in urine is more than 10 grams per litre, it may be determined by the saccharimeter. The direct reduction coefficient can only be obtained with boiled and filtered urine, as otherwise a certain quantity of cuprous oxide remains in suspension; two indirect reduction coefficients should be determined. (1) The coefficient of the original urine after treatment with mineral acid, and (2) the coefficient of the boiled and filtered urine when treated in the same manner. The difference between these coefficients gives the amount of mucin, &c.,

present, and the difference between the direct and indirect coefficients of the boiled and filtered urine gives the amount of glucosides.

J. J. S.

Estimation of Diabetic Sugar. By FRÉDÉRIC LANDOLPH (*Compt. rend.*, 1897, 125, 612—613).—The polaristrobometer alone indicates the real quantity of active diabetic sugar in a solution. The coefficient of reduction gives double or treble the amount of sugar indicated by the polaristrobometer. Determinations by the method of fermentation give results which vary greatly with the time that has elapsed between the end of the fermentation and the reading off of the volume of carbonic anhydride (compare Abstr., 1897, ii, 512).

C. H. B.

Quantitative Separation of Cellulose-like Carbohydrates in Vegetable Substances. By WILHELM HOFFMEISTER (*Landw. Versuchs-Stat.*, 1897, 48, 401—411. Compare Abstr., 1890, 581).—To separate the hemicelluloses, celluloses, and the constituents of lignin without essential change, the substance, after being freed from fat, is extracted with dilute hydrochloric acid and ammonia, and the residue frequently agitated for a day or two with 5—6 per cent. caustic soda solution. It is then diluted, the extract poured off, neutralised with hydrochloric acid, treated with sufficient alcohol, and the hemicellulose filtered, dried, and weighed. The residue from the soda extract is washed on a filter with hot water, and extracted with Schweizer's reagent.

When the final residue (lignin) is subjected to prolonged extraction with boiling dilute ammonia (a suitable apparatus is described, with sketch) until the ammonia is no longer coloured, a residue is obtained which mostly dissolves in Schweizer's reagent, and on repeating the process the residue is found to consist largely of mineral matter. The dissolved cellulose-like substances often contain considerable amounts of pentosans.

According to the nature of the substance, the extraction with ammonia may take weeks, or months, or even longer; the ammonia extracts of hard woods (as *Lignum vitæ*), and of cork, are dark brown, and give an odour of vanilla when evaporated down. The residues, which are insoluble in water, but redissolve in ammonia, have the properties of humic acids. Other vegetable substances, when extracted, yielded, besides humic acids, a compound, $C_6H_7O_2$, soluble in alcohol and chloroform, but insoluble in water, ether, and benzene; preparations from different sources melted between 200° and 210° .

N. H. J. M.

General and Physical Chemistry.

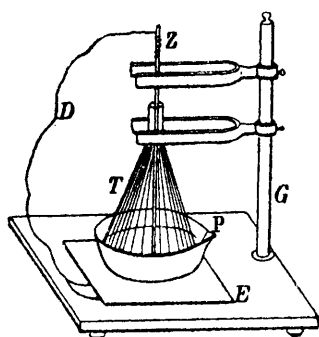
A New Agent for Increasing the Angle of Rotation. By PAUL WALDEN (*Ber.*, 1897, 30, 2889—2895).—Alkaline solutions of uranyl salts produce considerable increase in the angle of rotation of optically active substances dissolved in water or alcohol. The increase is associated with the presence of a hydroxylic group in the active substance, and reaches a maximum when the molecular proportion of hydroxy-compound to uranyl salt and alkali is 1 : 1 : 4.

In the case of *l*-malic acid, the angle of rotation is 500 times that exhibited by the original solution. M. O. F.

Influence of Altitude and Temperature on the Decomposition of Oxalic Acid by Light. By J. VALLOT and GABRIELLE VALLOT (*Compt. rend.*, 1897, 125, 857—858).—Experiments made at Chamounix (1095 m.) and at Montanvert (1925 m.) on the oxidation of solutions of oxalic acid by light, show that at the higher altitude the rate of change is much higher, the ratios of the amounts of decomposition at the two places varying from 1·5 to 2·9, with a mean of 2·1. The chemical activity of the light, therefore, increases very rapidly with the altitude. A considerable proportion of the chemically active rays is absorbed by even a comparatively thin layer of glass. In the course of the experiments, it was observed that, although heat alone does not decompose the oxalic acid solution, it very greatly accelerates the action of light.

The authors suggest that, in investigations into the laws of plant life, the combined effect of light and temperature must be considered rather than the effect of either of them alone. C. H. B.

Electrical Energy caused by the Direct Action of the Atmosphere. By HENRY N. WARREN (*Chem. News*, 1897, 76, 200).—Plates are prepared of a special porous compressed graphite, and about one-quarter of each plate is rendered active by immersion in platinic oxalate, drying and igniting in an atmosphere of hydrogen. In contact with a solution of ferrous sulphate, the platinum surface induces oxidation of the iron by the oxygen of the atmosphere. Several of these plates are attached to a circular lead beam, which surrounds a porous diaphragm containing as negative element a rod of amalgamated zinc, the carbons being so arranged as to allow the platinised portion to project above the solution, which consists of strongly acidified ferric sulphate. On completion of the circuit, a powerful current is at once generated, and continues until the complete reduction of the ferric salt has taken place, which naturally terminates the action. On now withdrawing the zinc, the platinum surface condensing the atmospheric oxygen steadily re-oxidises the ferrous salt, and thus renews the action when required. H. C.



Simple Electrolytic Apparatus. By A. GAWALOWSKI (*Chem. Centr.*, 1896, ii, 1075; from *Centralbl. Nahr. und Genussm.*, 2, 343).—The electrolyte is placed in a platinum dish, *P*, which stands on a nickel plate, *E*. A small funnel, *T*, is placed over the dish, and through the stem of this a zinc rod, *Z*, is introduced, the funnel and rod being supported in a vertical position by the stand, *G*. The wire, *D*, connects *Z* with *E* and closes the circuit.

H. C.

Metallic Sulphide Electrodes. By ISIDOR BERNFELD (*Zeit. physikal. Chem.*, 1898, 25, 46—73).—In electrolysis with electrodes of metallic sulphides, the following changes occur. (1) In acid solutions: at the anode, the metal is dissolved and the sulphur precipitated or oxidised; at the cathode, hydrogen sulphide is formed with separation of the metal; (2) in alkaline solutions: at the anode, the metal forms a hydroxide and the sulphur is oxidised; at the cathode, the metal is precipitated and the sulphur passes into solution as an ion. Lead sulphide was first employed for quantitative work, and it was observed that the resistance of this compound decreases with rise of temperature, although the conduction is purely metallic. In alkaline solutions, the quantity of lead precipitated and of sulphur dissolved at the cathode was found to be in complete accord with Faraday's law. The electrodes are best prepared electrolytically from pure lead, and by means of such electrodes a constant E. M. F. may be obtained in sodium sulphide solutions, if alteration in the latter is prevented by passing a continuous current of hydrogen sulphide. Measurements of the E. M. F. of lead sulphide in solutions of sodium sulphide at different concentrations, indicated the univalency of the ions, which the author hence considers to be $-\text{SH}$. The current passes from the more highly to the less concentrated solutions, and the changes occurring at the electrodes may be thus represented: $\text{PbS} + \text{SH}_2 \rightleftharpoons \text{Pb} + 2\text{SH}^-$, in the more dilute solution, therefore, two SH ions are formed and one undissociated SH_2 disappears, whilst the reverse obtains in the more concentrated solution. The E. M. F. is hence given by the equation $\pi = RT/\epsilon \times \log c_1/c - RT/2\epsilon \times \log c'_1/c'$, where c_1, c are the concentrations of the ions and c'_1, c' are the concentrations of the undissociated hydrogen sulphide. When the concentration of the hydrogen sulphide was kept constant, that is, $\log c'_1/c' = 0$, the E. M. F. was found to agree well with the calculated value. Further, by the use of equally concentrated sodium hydrosulphide solutions saturated with hydrogen sulphide at different pressures, an E. M. F. was obtained which agreed satisfactorily with the value calculated from the expression $\pi = -RT/2\epsilon \times \log c'_1/c_1$. By the use of electrodes of silver sulphide and of bismuth sulphide, similar results were obtained, so that, as the expression shows, the electromotive force is independent of the valency of the

metal. By the use of cells of the type : silver | N/1 silver nitrate | N/1 sodium hydrosulphide | silver sulphide, the solubility of the silver sulphide, &c., may be found ; the values thus obtained for the silver, lead, and bismuth sulphides are respectively 3.4×10^{-22} , 2.9×10^{-5} , and 2.1×10^{-26} . L. M. J.

Electrical Conductivity in Mixed Solutions of Electrolytes. By K. HOPFGARTNER (*Zeit. physikal. Chem.*, 1898, 25, 115—143).—In a solution of two different electrolytes, if n_1 and n_2 be the concentrations of the cations and u_1 , u_2 their migration velocities, then the ratio of the number of the respective cations passing in the same time across any section towards the cathode is given by $n_1 u_1 / n_2 u_2$. If this ratio, d_1/d_2 , be directly obtained from the alteration of the anode liquid, then if the migration velocities are known, the concentrations of the ions can be calculated $n_1/n_2 = u_2 d_1 / u_1 d_2$. The ratios of the concentrations of the hydrogen and sodium ions were thus obtained in the case of mixtures of equally concentrated solutions of sodium chloride and hydrogen chloride, and the values compared with those obtained by means of Rudolphi's expression. The agreement was satisfactory, indicating that the admixture of these highly dissociated solutions has little effect on the dissociation. In the case of mixtures of similar hydrogen chloride and barium chloride solutions, however, the agreement was not good, probably owing to the assumption that the dissociation of the barium chloride is entirely to Ba'' and Cl ions. The values of the transference ratios of the ions was also obtained for the three salts examined at different dilutions ; for sodium, the transference number increases with increasing dilution, whilst for both barium and hydrogen the reverse was found to obtain. The quantity of the cations deposited as a result of the purely electrical action was calculated from these numbers, and the results were found to agree well with the silver deposited in a voltameter included in the circuit. L. M. J.

Source of Error in the Determination of the Heat of Dissociation of Electrolytes. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1897, 24, 608—614).—The equilibrium equation in the case of a dissociation process is $c_2^x c_3^y / c_1 = k$, where x and y are the numbers of the different ions resulting from the dissociation. The concentrations c_1 , c_2 , and c_3 are given by the expressions $(1 - \alpha)c / (1 + \beta)$, $\alpha \alpha c / (1 + \beta)$, $y \alpha c / (1 + \beta)$, that is, are functions of β , the degree of dissociation of the solvent. Hence, since by temperature change the degrees of dissociation of both solute and solvent are directly altered, it follows that the degree of dissociation, α , of the solute undergoes, not only the direct change due to temperature, but also a secondary change due to the alteration of the concentration. On this account, the heat of dissociation is not accurately given by the ordinary expression $q = RT^2 d \log k / dt$, but by an extended expression, $RT^2 \{ d \log k / dt - (x + y - 1) d \log (1 + \beta) / dt \}$. In the case of potassium, the author shows that the omission of the second term leads to an error of 100 per cent., its value being calculated by the aid of Ramsay's determinations of the association factor of water at different temperatures. L. M. J.

Temperature Coefficient of the Potential of Calomel Electrodes, with various Dissolved Electrolytes. By ALBERT GOCKEL (*Zeit. physikal. Chem.*, 1897, 24, 703—704).—Richards, in his paper on the above subject (this vol., ii, 7), has completely overlooked the author's second paper (Abstr., 1894, ii, 78), in which several of Richards' results were previously obtained, and corrections had been made of the values given in the first paper, the only one cited by Richards.

L. M. J.

Thermoregulator. By F. FRIEDRICH (S. 36, 674).—This thermoregulator is very similar in principle to that of Reichardt, but has the inlet and outlet channels for the gas drilled obliquely through the plug of a stopcock, and meeting at the top of a mercury tube.

M. J. S.

New Method of Determining Melting Points. By MARIUS L. Q. VAN LEDDEN HULSEBOSCH (*Zeit. anal. Chem.*, 1897, 36, 685—686; from *Pharm. Centralhalle*, 37, 231).—In a case in which the small amount of the material, and the presence of adhering wool, precluded the use of the capillary tube, the substance was placed in an aluminium vessel, shaped like a watch-glass, floating on water in a beaker which was warmed in a water bath. The substance was watched through a lens, and the water temperature observed at the moment when the change in the lustre of the powder indicated that the melting point was reached.

M. J. S.

Gradual Change and Thermodynamics. A Correction. By PIERRE DUHEM (*Zeit. physikal. Chem.*, 1897, 24, 666).—The author corrects an erroneous differential equation which occurs in his paper on the above subject (Abstr., 1897, ii, 439), but which does not affect the deductions obtained by its use.

L. M. J.

The Relation between the Heat of Solution, Solubility, and Dissociation. By HEINRICH GOLDSCHMIDT and GERTRUD VAN MAARSEVEEN (*Zeit. physikal. Chem.*, 1898, 25, 91—99).—The expressions deduced by van't Hoff (1) and by van Laar (2) for the heat of solution of a binary electrolyte are respectively (1) $d\log c/dt = Q/2(1 + a)T^2$ and (2) $d\log c/dt = Q(2 - a)/4T^2$ (Abstr., 1895, ii, 484). As Rudolphi, when determining the heat of the solution of some silver salts (Abstr., 1895, ii, 435), did not determine the solubilities, the authors have redetermined the solubilities, degrees of dissociation,

	Found.	Calc. 1.	Calc. 2.
Silver acetate	- 4613	- 4828	- 4369
„ propionate.....	- 3980	- 4155	- 3789
„ isobutyrate	- 2860	- 3010	- 2715
„ orthonitrobenzoate.	- 7083	- 7925	- 7167

and heat of solutions of the saturated solutions of silver acetate, propionate, isobutyrate, and orthonitrobenzoate. The degree of dis-

sociation was calculated from the conductivity, and the heat of dissolution of the salts obtained directly by their precipitation from solution in a platinum calorimeter. The values obtained in this way are compared with those calculated, using the above formulæ. It is seen from the accompanying table that neither formula is entirely satisfactory, the values obtained experimentally lying between those given by the two formulæ.

L. M. J.

Condensation and Critical Phenomena of Mixtures of Two Compounds. By J. P. KUENEN (*Zeit. physikal. Chem.*, 1897, 24, 667—696).—See Abstr., 1896, ii, 10; 1897, ii, 544.

Association or Dissociation ? By HANS JAHN (*Ber.*, 1897, 30, 2982—2993).—A reply to the objections which have been put forward by Crompton (*Trans.*, 1897, 925) and Traube (this vol., ii, 109) to the theory of electrolytic dissociation. The author maintains that Crompton's objections have been already dealt with by Planck, and have been satisfactorily and completely removed by him in his thermodynamical treatment of the subject (see Planck's *Vorlesungen über Thermodynamik*). Traube's view that combination takes place between the solvent and the dissolved substance, and that in the case of non-electrolytes one molecule of the dissolved substance always unites with but one molecule of the solvent, is improbable. It does not serve to explain the facts, as the formula of Poynting, on which Traube bases his further conclusions, is incorrect. It also necessitates the assumptions that, in the case of electrolytes, one molecule of the dissolved substance enters into combination with a greater and greater quantity of water as the dilution increases, and that the molecular conductivity of electrolytes does not alter with the concentration.

H. C.

Dissociation of Nitric Peroxide. By K. SCHREBER (*Zeit. physikal. Chem.*, 1897, 24, 651—665).—If the dissociation of nitrogen peroxide be represented by $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, then the equilibrium constant is given by the equation $k = c_2^2/c_1 = a.e^{-b/T}.T/p$, where c_2 and c_1 are the concentrations of the complex and simple molecules, and a and b are constants. If γ be the degree of dissociation, $c_2 = 2\gamma/(1 + \gamma)$ and $c_1 = (1 - \gamma)/(1 + \gamma)$, and if D and d be the densities of the N_2O_4 and the actual gas $\gamma = (D - d)/d$. The above equation then reduces to $4(D - d)^2/D^2(d - D) = a.e^{-b/T}.T/p$, and the author investigated Natanson's determinations of the density (Abstr., 1885, 862; 1886, 657) in order to find whether the observations are in accord with this relationship. Allowing experimental errors of $\frac{1}{3}$ per cent. in the densities of the dissociated gas, and of 0.1 per cent. in the density of the N_2O_4 , the possible error in the degree of dissociation is calculated for each of Natanson's experiments. In some cases, the error is found to exceed 100 per cent., and only those experiments where it is less than 10 per cent. are used for comparison with the theory. It is thus found that, at equal temperatures, the value kp is approximately constant, and that it increases rapidly with the temperature. Expressing the relationship in the form $\log(kp/T) = \log a - b(\log e)/T$, it was found that the values of kp are fairly accu-

rately reproduced by the use of the constants $\log a = 9.13242$ and $b \log e = 2866.2$. The dissociation is hence considered to proceed normally and in accord with theory. From the value of the temperature coefficient of the dissociation degree, the value $13132 + 2T$ is obtained for the heat of dissociation, a result in close accord with that calculated by van't Hoff from Deville and Troost's experiments, namely, 12900. The apparent specific heat of the gas had been determined by Berthelot and Ogier, and from these results, allowing for the thermal effects of the dissociation changes, the author obtains the following values for the molecular heats.

	c_p .	c_v .	c_p/c_v .
N_2O_4	14.85	12.85	1.155
NO_2	8.43	6.43	1.31

These results are in accord with the experimental determination of the ratio of the specific heats, namely, 1.17 for 84 per cent. N_2O_4 , and 1.31 for NO_2 (by extrapolation).

L. M. J.

Dissociation in Mixed Salt Solutions. By ANDREAS FOCK (*Zeit. physikal. Chem.*, 1898, 25, 74—78).—The author further contests the validity of Nernst's solubility law (Abstr., 1897, ii, 481). The solubility of mixed crystals of potassium and ammonium chlorides is also considered. Representing the concentration of the ammonium chloride in the solutions and crystals by c and x respectively, then from the values of c/x the value of the dissociation γ is calculated which leads to a constant ratio for $c(1 - \gamma)/x$, the equilibrium ratio if the salt is undissociated in the solid. From this value of γ , the ratio $c\gamma/\sqrt{x}$ is obtained, leading to a value which is constant, within the limits of experimental errors, so that the partition law is valid for such solutions.

L. M. J.

Dissociation of Compounds Dissolved in Mixtures of Alcohol and Water. By ERNST COHEN (*Zeit. physikal. Chem.*, 1898, 25, 1—45). In order to completely investigate the dissociation of compounds dissolved in aqueous alcohol, the author determined the electrical conductivity of solutions of potassium iodide, the dilution varying from 64 to 2048, and the alcoholic content from 0 to 100 per cent. (volume); the apparatus and the method of preparation of the solutions are fully described. It is noteworthy that, at dilutions above 512, the conductivity in absolute alcohol is greater than that in 80 per cent. alcohol, whereas at lower concentrations the reverse obtains, so that in the former case the addition of water lowers the conductivity. If the conductivity of the alcoholic solution be referred to that of the pure aqueous solution at equal dilution, it is found that the value obtained depends only on the alcoholic content and not on the dilution. This holds for solutions containing less than 80 per cent. of alcohol, but above this value the ratio increases with dilution. By examination of Wakeman's results (Abstr., 1893, ii, 257), it is found

that the same constancy obtains for solutions of potassium chloride, sodium chloride, hydrogen chloride, and sodium acetate, whilst the experiments of Walker and Hambly (*Trans.*, 1897, 72) show that, below 50 per cent. of alcohol, the same result obtains for solutions of diethylammonium chloride. From this, it follows that the molecular conductivity of a solution in aqueous alcohol may be obtained from that of the equivalent aqueous solution by multiplying by a factor which is independent of the dilution. These factors are given for the various salts examined, and it is further seen that the factor is independent of the nature of the dissolved salt, and depends solely on the alcoholic content, being but little, if at all, affected by changes of temperature. As this result may be extended to infinite dilution, it follows that substances which obey the dilution law in aqueous solution do so also in solutions in aqueous alcohol, and conversely. As the degree of dissociation in aqueous solution is given by the expression $\alpha = \mu_v / \mu_\infty$, that in the solution in aqueous alcohol is obtained by the expression $\alpha_1 = k\mu_v / k\mu_\infty$, and hence $\alpha_1 = \alpha$; the replacement of water by alcohol, therefore, has no effect on the degree of dissociation of the dissolved material. The velocity of inversion of cane-sugar by hydrogen chloride is, however, diminished by the addition of alcohol, that is, the dissociation is decreased; the author hence considers it doubtful whether the electrical conductivity affords a trustworthy measure of the dissociation.

L. M. J.

Dissociation of Dibasic Organic Acids. I. By W. A. SMITH (*Zeit. physikal. Chem.*, 1898, 25, 144—177).—An expression was obtained by Noyes for the dissociation of the acid ion of the acid salt of a weak dibasic acid (*Abstr.*, 1893, ii, 365), and the laws were enunciated that, (1) the hydrogen dissociation decreases with proximity of the acid groups, (2) the introduction of new groups influences the dissociation of the acid and of the acid salt in the same manner; the author endeavours to see to what extent these laws are valid. The method of sugar inversion as a means of measuring the hydrogen ion concentration was first studied. At 100°, the rotation of sugar solutions in pure water rapidly changes, the change being partly due to inversion and partly to decomposition; it is, moreover, irregular, so that different experiments give different results, but on adding hydrogen sodium succinate, the rate of inversion becomes perfectly regular, the disturbing influences of the pure water being eliminated; in this case, the inversion is due entirely to the hydrogen ions. Neutral salts of weak acids have a similar protective influence, and the sugar changes only very slowly, whereas the salts of strong acids give curves of inversion which, like those due to water, are irregular. With completely dissociated hydrochloric acid, a perfectly satisfactory equation constant was obtained, and experiments were then performed to ascertain whether the velocity of inversion is proportional to the concentration of the hydrogen ions; this was found to be accurately the case for highly dissociated compounds, but with weakly dissociated compounds this proportionality apparently did not exist, the values for the dissociation being obtained from the conductivity experiments of Ostwald and Kohlrausch. As the ratio of the inversion velocity to

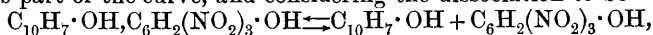
hydrogen concentration only slowly decreases with dilution in the case of the organic acids, it follows that the undissociated acid has but slight influence on the inversion, whereas the influence of the undissociated hydrochloric acid is very considerable. L. M. J.

Equilibrium between Ammonium Nitrate and Ammonia. By BASIL B. KURILOFF (*Zeit. physikal. Chem.*, 1898, 25, 107—111).—Dry ammonia is absorbed by ammonium nitrate with the formation of a liquid which has been, by various observers, supposed to consist of different additive compounds of the two substances. The author's observations on the dissociation pressure of the liquid had previously led to the supposition that no such compound existed, but that the liquid was a solution of the nitrate in ammonia. In order to test the accuracy of this view, the author has determined the composition of the liquid, which is in equilibrium with a solid phase at temperatures ranging from about -80° to $+168^{\circ}$. The curve indicates the existence of a solid phase, probably $\text{NH}_4\cdot\text{NO}_3\cdot 3\text{NH}_3$, at temperatures below -40° , but above this temperature the curve is perfectly unbroken, being the curve of equilibrium between solid ammonium nitrate and the solution, so that above -40° no compound of the two components exists. L. M. J.

Equilibrium in the Systems, Ether-water and Ether-water-malonic Acid. By EDUARD A. KLOBBIE (*Zeit. physikal. Chem.*, 1897, 24, 615—632).—The equilibrium of water and ether was first determined, the composition of the two layers being found at temperatures varying from -4° to $+95^{\circ}$. Between these limits, the percentage of water in the upper layer increased from 0.94 to 2.71, whilst between -4° and 82° the percentage of ether in the lower layer decreased from 12.63 to 2.7. Above about 80° , however, the percentage again increases, as no turbidity is caused by heating a liquid with 2.5 per cent. of ether, whilst a 2.7 per cent. solution, which becomes turbid at about 82° , is again clear at 115° . The solubility of malonic acid in water and ether was determined at temperatures varying from 0° to 132° , the melting point of the acid, after which the composition was found of the two layers formed when malonic acid is added to ether and water at 15° ; the conjugate points of the binodal curve are thus obtained. The composition of the liquid in equilibrium with the solid acid was also found, and the equilibrium field is thus divided into three regions, where exist, (1) two liquid phases, (2) homogeneous liquid, (3) liquid and solid phase, and the composition of the phase for any original mixture is readily obtained from the diagram. The partition coefficient of the acid is not constant, a result which must necessarily obtain since the compositions of the solvents alter on the addition of the acid. By graphical extrapolation, however, the limiting value of 7 is found, which is still not the partition coefficient between ether and water but between the two ether-water solutions. L. M. J.

Application of the Law of Mass-action to Researches on the Equilibrium between β -Naphthol and Picric Acid in Benzene Solution. By BASIL B. KURILOFF (*Zeit. physikal. Chem.*, 1897, 24, 697—702).—In the author's experiments on the equilibrium of

solutions containing the above three components (this vol., ii, 112), the greater portion of the isotherm for 29.5° corresponds with the naphthol-picrate solid phase. The mass-action law may be applied to this part of the curve, and considering the dissociation to be



then if dissociation be complete, the product of the concentration of the components should be constant. This is not actually the case, but as the product only varies slightly, the dissociation is probably very considerable. Calculations of the degree of dissociation and of the dissociation constant are made, but the agreement of the values for the latter is not satisfactory. Evidence of the high dissociation is also obtained from the cryoscopic and boiling point observations, which lead to a molecular weight of about 195, in place of 373, and hence indicate dissociation to the extent 0.88. The author also points out that cryoscopic observations do not indicate the formation of compounds between solvent and solute, so that any indication of the formation of hydrates is only obtainable when solvents other than water are employed. (Compare Abstr., 1897, ii, 397.) L. M. J.

Aqueous Solutions of Two Salts with One Common Ion.
By C. HOITSEMA (*Zeit. physikal. Chem.*, 1897, 24, 577—607).—Representing the salts by XY and ZY, then in a saturated solution of the former, if A is the total concentration and d the degree of dissociation, $A(1-d) = kA^2d^2 = \text{constant}$. If ZY be added and x, y, z , be the concentrations of the respective ions, and a that of the salt ZY, of which d_2 is the degree of dissociation, then the equations of equilibrium are $xy = A^2d^2$; $(a-z)/zy = a(1-d_2)/a^2d_2^2$; $x+z=y$ and the total solubility of XY = $x + A(1-d)$ affords a means of ascertaining the validity of the results. It follows from these equations that the concentration of XY must fall on the addition of ZY, but cannot sink below the value $A(1-d)$, remaining constant when this minimum is reached. Three types of curves are thus obtainable where the solubility of (1) neither salt, (2) one of the salts, (3) both salts reaches this minimum. In some cases, however, the addition of ZY is known to cause either an immediate increase in solubility or a decrease followed by an increase, and in such cases reactions occur between XY and ZY. The author first considers the effect of the formation of a *double salt*, that is, a compound XY₂ZY which dissociates into XY and ZY. The equations of equilibrium are obtained, and it is seen that addition of ZY must at first cause a decrease of solubility of XY, but that, as formation of the double salt increases, the solubility may reach a minimum and afterwards increase, and the forms of the curves are given for the several cases in which (1) ZY, (2) XZY₂ first reaches its saturation concentration. In the case where *complex salts* are formed, the effects are different, the term complex salt being restricted to the compound dissociating into new ions, X and ZY₂ (Morgan, Abstr., 1895, ii, 478; Kahlenberg, Abstr., 1896, ii, 6). In this case, at first no ZY molecules exist in solution, and hence no Y ions. The solubility of XY, therefore, increases until the saturation concentration of X(ZY₂) is reached, after which it decreases owing to the precipitation of this solid. A similar result is obtainable for the

effect of XY on the solubility of ZY, so that the complete curve consists of four parts corresponding with the solid phases XY, X(ZY₂), Z(ZY₂), ZY. When mixed crystals are formed, the conditions of equilibrium are more complicated, owing to changes in the solid phase. If the composition of the crystals changes continuously, a continuous curve is obtained, which may or may not exhibit maxima and minima, but if the composition of the crystals changes abruptly at definite concentrations, curves of at least two distinct parts result, which may be further complicated by the existence of double salts. L. M. J.

Solubility and Decomposition of Double Salts in Water. By EBERHARD RIMBACH (*Ber.*, 1897, 30, 3073—3089).—The crystallographic properties and solubilities of the double cadmium chlorides investigated are given below.

Salt.	Cryst. system.	Solubility.
1. NH ₄ Cl, CdCl ₂	Rhombic	^{105°} _{2.4°} P = 29.88 + 0.2144 t.
2. 4NH ₄ Cl, CdCl ₂	Hexagonal	Is decomposed.
3. KCl, CdCl ₂ + H ₂ O	Monoclinic	^{105°} _{2.6°} P = 22.20 + 0.2901 t.
4. 4KCl, CdCl ₂	Hexagonal	Is decomposed.
5. BaCl ₂ , 2CdCl ₂ + 5H ₂ O ..	Regular	^{107°} _{22.5°} P = 40.80 + 0.1988 t.
6. BaCl ₂ , CdCl ₂ + 4H ₂ O ...	Triclinic	^{109°} _{22.5°} P = 35.78 + 0.2678 t.
7. MgCl ₂ , 2CdCl ₂ + 12H ₂ O	Rhombic	^{121°} _{2.4°} P = 45.98 + 0.16505 t.

Double chlorides of the type 4MCl, CdCl₂ are decomposed by water according to the equation 4MCl, CdCl₂ ⇌ MCl, CdCl₂ + 3MCl. The reaction proceeds in the direction right to left with an increase of temperature, but in the reverse direction as the temperature sinks. On diffusion, the double chlorides, Nos. 5, 6, and 7, undergo decomposition, and in all cases the cadmium chloride passes through the membrane less readily than the other constituent.

On comparing the solubilities of the double salts with those of their constituents, it is found that the value dp/dt (that is, the increase in solubility with the temperature) is much greater for the double salts than for their constituents. The solubility of any of the double chlorides at 0° always lies between the solubilities of its two constituents at that temperature. J. J. S.

Validity of the Dilution Law. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1898, 25, 79—90).—The author, in considering the causes of the divergences from Ostwald's dilution law which are exhibited by many aqueous and alcoholic solutions, is led to the important conclusion that, although the ratio μ_v/μ_∞ yields a degree of dissociation, yet this value is not that which obtains in the absence of the current; the dissociation thus determined is, therefore, incorrect. The cause of the alteration of the dissociation during the passage of the current is, in the author's opinion, the great difference which exists between the temperature of the actual conducting ions and the salt molecules, and that of the liquid as a whole. L. M. J.

Transition Point of a Solid Solution. By VICTOR ROTHMUND (*Zeit. Physikal. Chem.*, 1897, 24, 705—720).—The author first shows that, in the case of a solid solution, the effect of the solute on a

transition temperature of the solvent is completely analogous to the cryoscopic effect in a liquid solution. The depression of the transition temperature is hence given by the equation $t_0 - t_1 = RT^2/\phi \cdot (c_2 - c_1)$, where ϕ is the heat of transition and c_2, c_1 the concentrations of the solute in the two solid phases. If n be the ratio of the molecular weights of the solute in the two solutions, then $c_1/c_2^n = k$, so that for the case where the molecular weights are equal, $t_0 - t_1 = RT^2/\phi \cdot c_2(1 - k)$; that is, the lowering of the transition temperature is proportional to the concentration of the solute, a result which does not obtain, however, if the molecular weights differ. Experiments were made with solutions of carbon tetrachloride in carbon tetrabromide, in which cases solid solutions are formed, whilst the bromide exists as monoclinic and regular crystals with a transition point of about 46° . The temperature was determined by a thermometric method which practically amounts to the observation of a break in the curve of cooling. The solid solutions of the two compounds were obtained by precipitating their solution in alcohol by means of water, but, as the composition of the precipitate was not identical with that of the mixture dissolved originally, corrections for the depression of the transition point had to be applied, these corrections being experimentally obtained by redissolving the precipitate and again performing the experiment. The results indicate a constant value for the molecular depression and hence that the tetrachloride possesses the same molecular weight in the two solid solutions. As, further, the molecular structures of isomorphous compounds are similar, it follows that the two modifications of the tetrabromide possess equal molecular weight, so that the polymorphism is not due to polymerism.

L. M. J.

Elementary Chemical Considerations. By F. WALD (*Zeit. physikal. Chem.*, 1897, 24, 633—650).—The author, in continuation of previous papers, endeavours to show that no necessity exists for the assumption of the atomic hypothesis for the explanation of chemical phenomena. He considers the case of a chemical operation (an analysis) undertaken with the aid of materials the composition and nature of which are completely unknown, and shows that the chemist is guided, although perhaps unconsciously, by a phase law which he calls the $(N+1)$ rule; he gives definitions, based upon Gibbs' phase law, of identical and dissimilar materials and of a chemical compound (*Abstr.*, 1897, ii, 308).

L. M. J.

Inorganic Chemistry.

Reduction of Sulphurous Acid to Hydrogen Sulphide. By EDUARD DONATH (*Zeit. anal. Chem.*, 1897, **36**, 663—665).—Sulphurous acid is readily reduced to hydrogen sulphide by a hot solution of stannous chloride strongly acidified with hydrochloric acid. The

sulphurous acid or sulphite solution must be added slowly, or the hydrogen sulphide formed will react with sulphurous anhydride, causing separation of sulphur. This fact may be applied to the detection of arsenic and antimony in presence of much tin. A further quantity of strongly acid stannous chloride is added, and to the boiling liquid a solution of sodium sulphite or sulphurous acid is added in drops. Arsenious and antimonious sulphides are precipitated, the tin is not. The same method may be applied to the detection of arsenic in commercial sulphuric acid.

M. J. S.

Action of Hydrogen on Sulphuric Acid. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, 125, 743—746).—A slow current of hydrogen can be passed for an hour through concentrated sulphuric acid at the ordinary temperature without any appreciable production of sulphurous anhydride, but if contact between the gas and the acid is prolonged, the gas is absorbed and the acid is reduced. Light has no distinct influence on the reaction. Dilute sulphuric acid is not reduced by the hydrogen. At 250°, with the concentrated acid, reduction takes place somewhat rapidly, especially in presence of a considerable excess of acid. When mixtures of hydrogen and oxygen are left in contact with sulphuric acid either at the ordinary temperature or at 250°, both gases are absorbed, but the rate of absorption of hydrogen is the same as in the absence of oxygen, and the absorption of oxygen is due to its combination with the sulphurous anhydride that is formed. Dry hydrogen and sulphurous anhydride do not interact at 100° or 280°.

The reduction of concentrated sulphuric acid by hydrogen is an exothermic reaction and develops + 15.1 Cal., this value being increased to + 30.1 Cal. in presence of a large excess of sulphuric acid, owing to the heat of hydration. In the case of dilute sulphuric acid, the reaction would be endothermic.

C. H. B.

Phosphorous Oxychloride. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, 125, 771—772).—The action of a small quantity of water, whether in the liquid form, or as atmospheric moisture, on phosphorus trichloride, produces *phosphorous oxychloride*, POCl_3 , which is isolated by distilling off the trichloride, at first on a water bath and finally under low pressure. This oxychloride is a yellowish, hyaline solid of the consistence of paraffin, with an odour recalling that of the oxychloride, POCl_3 . It is very hygroscopic, and dissolves in water with a strident noise, the products being hydrochloric acid, phosphorous acid, and a small quantity of an amorphous yellow solid. It is rapidly decomposed by light with formation of a pale yellow precipitate which changes to reddish-yellow if the action of light is prolonged. The oxychloride is insoluble in most solvents, but dissolves in phosphorus trichloride. It combines slowly with chlorine, and yields phosphoric oxychloride, POCl_3 .

The yield of phosphorous oxychloride is always very small, probably because its formation is limited by its extremely hygroscopic nature.

C. H. B.

Evolution of Helium from a Natural Compound with Production of Heat and Light. By JULIUS THOMSEN (*Zeit. physikal. Chem.*, 1898, 25, 112—114).—Many years ago, the author observed the production of light and heat when a mineral occurring among the cryolite beds was raised to a low red heat. The mineral consists chiefly of calcium fluoride with a small quantity of the fluorides of cerium and yttrium, and by heating in a vacuous tube it was found that helium was evolved, together with some hydrocarbon. The helium may also be obtained by heating the powdered mineral with copper oxide and absorbing the carbonic anhydride. Experiments were also undertaken to determine whether the evolution of helium also accompanied the luminosity observed on heating specimens of fluor spar, but the results were negative. L. M. J.

Ammonium Peroxide. By PETR G. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 1897, 30, 3144—3146).—The authors' investigation of the salts of peruranic acid (this vol., ii, 165) has rendered it probable that these are compounds of metallic peroxides with peruranic acid. If this view is correct, the hydrogen ammonium salt is a compound of the acid with ammonium peroxide, a substance which has not been hitherto obtained. The present paper gives evidence of the existence of this substance.

When a concentrated, ethereal solution of hydrogen peroxide at -20° acts on an ethereal solution of ammonia at the same temperature, a heavy, viscous liquid separates in quantity depending on the temperature of the mixture; the odour of ammonia diminishes in strength, although the heavy liquid, owing to partial dissociation, has a faint odour of ammonia after careful washing with cooled ether. Ammonium peroxide is strongly alkaline, and when treated with caustic potash yields ammonia and potassium peroxide; it dissociates readily into ammonia and hydrogen peroxide, which is also formed under the influence of dilute sulphuric acid. It irritates the skin, on which it produces white stains; it is insoluble in ether, but dissolves readily in alcohol. An aqueous solution liberates oxygen, at first slowly, then very vigorously, a small proportion of ammonium nitrite being formed.

If the ethereal mixture of ammonia and hydrogen peroxide is cooled in solid carbonic anhydride, acicular leaflets separate, consisting of a compound of ammonium peroxide and hydrogen peroxide, of the composition $(\text{NH}_4)_2\text{O}_2 \cdot 2\text{H}_2\text{O}_2 + 10\text{H}_2\text{O}$. M. O. F.

Preparation of Carbides by the Action of Calcium Carbide on Oxides. By HENRI MOISSAN (*Compt. rend.*, 1897, 125, 839—844).—When calcium carbide is fused in the electric furnace with certain metallic and non-metallic oxides, the corresponding carbides are obtained usually in a crystalline form. Aluminium oxide yields the carbide C_3Al_4 , in yellow crystals; trimanganese tetroxide, the carbide CMn_3 ; chromic oxide, the carbide C_2Cr_3 ; molybdenum dioxide, the carbide CMo_2 ; tungstic anhydride, the carbide CW_2 ; titanium dioxide, the carbide CTi , and silica yields silicon carbide. Lead, bismuth, and tin oxides, and oxides of other metals that do not form definite carbides,

are reduced to the metallic state. In all cases, the calcium carbide is converted into the oxide, but the latter is reconverted into carbide by the carbon of the crucible in which the substances are heated.

C. H. B.

Preparation of Strontium Sulphide by the Action of Hydrogen Sulphide on the Oxide or Carbonate. By JOSÉ R. MOURELO (*Compt. rend.*, 1897, 125, 775—777).—Strontium sulphide, SrS , is readily obtained as a white solid by the action of hydrogen sulphide on the red-hot oxide or carbonate, the latter, on the whole, giving the best results. Since the reaction is reversible, attention to the temperature and the rapidity of the current of gas is essential. If the conditions are such that the water formed can condense on the hot solid, the product contains some hydroxide. At a bright red heat, and with a slow current of gas, the product also contains strontium hydroxide, but with a sufficiently rapid current of gas, the conversion into sulphide is complete.

C. H. B.

Metallic Triple Nitrites. By CARL PRZIBYLLA (*Zeit. anorg. Chem.*, 1897, 15, 419—446).—*Copper lead ammonium nitrite* $\text{CuPb}(\text{NH}_4)_2(\text{NO}_2)_6$, obtained by adding a solution of copper and lead nitrate to a solution of ammonium nitrate and sodium nitrite, is a black, crystalline salt having a bluish, metallic lustre; it is stable at the ordinary temperature or when gently warmed, and is very similar to the corresponding potassium salt. Like this salt, all the other triple nitrites contain 6NO_2 .

Copper calcium potassium nitrite, obtained by mixing a well-cooled solution of copper chloride and sodium nitrite with a solution of potassium chloride, calcium chloride, and sodium nitrite, is a deep green, crystalline powder, which is purified by washing with 85 per cent. alcohol and then with alcohol.

Copper calcium ammonium nitrite, prepared in a similar manner to the preceding salt but using very concentrated solutions, closely resembles the potassium salt, but if kept, gradually decomposes with evolution of nitrogen trioxide.

Copper barium potassium nitrite, obtained by mixing a well-cooled concentrated solution of barium chloride and sodium nitrite with a solution of copper chloride, potassium chloride, and sodium nitrite, is also a deep green, crystalline powder; it is stable when kept dry, but decomposes on recrystallisation, with evolution of nitrogen trioxide and the formation of basic salts.

Copper barium ammonium nitrite is very similar to the potassium salt, but slowly decomposes when allowed to remain at the ordinary temperature.

Copper strontium potassium nitrite, $\text{CuSrK}_2(\text{NO}_2)_6$, is obtained in a similar manner to the preceding salts, but a large excess of strontium chloride should be employed, as otherwise a mixture of salts is obtained containing less strontium; these cannot be purified by recrystallisation. The corresponding *ammonium* salt is very similar to the potassium salt.

Nickel lead potassium nitrite, obtained by mixing dilute solutions of potassium, lead, and nickel nitrate with a slight excess of sodium

nitrite, is a heavy, brownish-yellow powder. The corresponding ammonium salt, which is a brownish-yellow powder, cannot be obtained pure. Salts containing nickel, barium, and ammonium nitrites, nickel, strontium, and ammonium nitrites and nickel, calcium and ammonium nitrites, are also described, but they are evidently mixtures.

Iron lead potassium nitrite is obtained on adding a solution of ferrous and lead nitrates to a solution of potassium nitrate and sodium nitrite as a heavy, reddish-yellow precipitate; this, after being washed by decantation with water, and then on a filter with alcohol, is an intense orange-yellow powder, insoluble in cold water and stable at the ordinary temperature.

Iron barium potassium nitrite.—A bright yellow precipitate which is apparently a mixture of salts is obtained on mixing equivalent quantities of ferrous chloride, barium chloride, and potassium chloride with the necessary quantity of sodium nitrite; by varying the proportions of the metallic salts, various mixtures of salts are obtained. A compound of the formula $\text{FeBaK}_2(\text{NO}_2)_6$ is obtained by mixing a solution of ferrous chloride [12.5 c.c. (1 c.c. = 0.1943 gram Fe)], potassium chloride (13 grams), and crystallised barium chloride (22 grams) in 120 c.c. of water with 100 c.c. of a solution of sodium nitrite (10 c.c. = 5 grams sodium nitrite); the precipitate is quickly separated by filtration, washed with alcohol, and dried at a gentle heat.

Iron calcium potassium nitrite and *iron strontium potassium nitrite*.—Yellow to reddish-yellow precipitates containing the three nitrites are obtained in a similar manner to the above salts; but they contain varying proportions of each nitrite according to the relative amounts of the constituents employed. The author was unable to obtain a compound to which a simple formula could be assigned. The corresponding ammonium salts of iron nitrite can be obtained in a similar manner by employing small quantities of the constituents for each experiment; they are very similar to the potassium salts.

E. C. R.

Action of Hydracids and Oxygen on Mercury and other Metals. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, 125, 746—749).—Hydrogen chloride may remain in contact with mercury at the ordinary temperature for many years without appreciable change. In sealed tubes, no reaction takes place below 500°. If, on the other hand, a mixture of dry hydrogen chloride (2 vols.) and oxygen (1 vol.) is allowed to remain in contact with mercury at about 20°, the hydrogen chloride gradually and completely disappears and the greater part of the oxygen is absorbed also, a mixture of mercurous chloride and oxychloride being formed. If mercurous chloride alone were formed, the reaction would develop + 87.6 Cal., but, nevertheless, the change takes place very slowly. Water does not prevent the reaction, but retards it to an extent depending on the proportion of water present. If hydrogen is added to the mixture of hydrogen chloride and oxygen, it remains unabsorbed, and the reaction with the mercury does not set up any reaction between the hydrogen and oxygen.

The action of hydrogen chloride and oxygen on mercury is analogous to the reactions observed with silver, lead, and copper.

When a mixture of hydrogen sulphide and oxygen is left in contact with mercury, the surface of the latter is slowly converted into sulphide, but the reaction does not continue unless the surface of the mercury is constantly renewed. The complete reaction would develop +74.8 Cal.

C. H. B.

Action of Sulphuric Acid on Mercury at the Ordinary Temperature. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, 125, 749—750).—When mercury is agitated with concentrated sulphuric acid at the ordinary temperature, the acid is partially reduced, and a mercury sulphate is formed which is precipitated as a basic salt when the acid is diluted with water. A minute quantity of black mercury sulphide is formed at the same time. The mercury used was very pure, and the same reactions were observed when the same quantity of mercury was subjected to three successive treatments with the acid. After prolonged contact between the acid and the mercury, the sulphate separates in yellowish crystals. A small quantity of water is sufficient to prevent the reaction; the acid $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ does not attack mercury.

C. H. B.

Cerium. By O. BOUDOUARD (*Compt. rend.*, 1897, 125, 772—774).—Experiments made with cerium acetate and sulphate tend to confirm Schützenberger's conclusion that cerium oxide free from thorium contains small quantities of an element of lower atomic weight. When the acetate is precipitated with hydrogen peroxide, the atomic weight of the element in the precipitate varies from 137.15 to 137.6, whilst the atomic weight of the element in the mother liquor varies between 137.85 and 139.9.

C. H. B.

Manganimolybdates. By ARTHUR ROSENHEIM and HERRMANN ITZIG (*Zeit. anorg. Chem.*, 1898, 16, 76—82).—The authors have prepared the complex salts described by Péchard (*Abstr.*, 1897, 11, 498) to which he assigns the composition $3\text{M}'_2\text{O}, \text{MnO}_2, 12\text{MO}_3$. They find that the ammonium salt described by Péchard is an *ammonium potassium manganimolybdate* of the composition $2(\text{NH}_4)_2\text{O}, \text{K}_2\text{O}, \text{Mn}_2\text{O}_3, 10\text{MoO}_3 + 5\text{H}_2\text{O}$. It is obtained by the action of potassium permanganate on ammonium manganimolybdate, and crystallises in dull-red, quadratic tablets; it is sparingly soluble in cold water, easily so in water at 70—80°, and decomposes when the solution is boiled, manganese dioxide being precipitated.

Potassium manganimolybdate, $3\text{K}_2\text{O}, \text{MnO}_2, 8\text{MoO}_3 + 5\text{H}_2\text{O}$, is obtained by the action of potassium permanganate on a solution of potassium paramolybdate, by adding potassium chloride to a mixture of potassium permanganate and sodium paramolybdate, or by adding potassium chloride to a solution of the preceding ammonium salt; the second and third methods give very good yields. It crystallises in yellowish-red, quadratic tablets, and is almost insoluble in water.

The sodium salt, which is extremely soluble, cannot be prepared in a pure state, but crystallises mixed with manganous salts and alkali molybdates. The free acid was obtained as a black mass. Neither of the preparations were fit for analysis.

The authors especially draw attention to the remarkable decomposition of the above ammonium salt with potassium chloride, which takes place quantitatively when a solution of the ammonium salt is mixed with an excess of potassium chloride solution and allowed to remain 12 hours at the ordinary temperature. An examination of the filtrate from the precipitated potassium salt shows that this decomposition takes place according to the equation

$$2(\text{NH}_4)_2\text{O}, \text{K}_2\text{O}, \text{Mn}_2\text{O}_3, 10\text{MoO}_3 + 4\text{KCl} = 3\text{K}_2\text{O}, \text{MnO}_2, 8\text{MoO}_3 + 4\text{NH}_4\text{Cl} + \text{MnO}, 2\text{MoO}_3.$$

E. C. R.

Peruranic Acid and its Salts. By PETR G. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 1897, 30, 2902—2907).—Of the two formulæ for peruranic acid put forward by Fairley (this Journal, 1877, i, 127), Mendeléeff regards the expression UO_4 as the more probable, the salts being represented by the formulæ $(\text{R}_2\text{O}_2)_2\text{UO}_4$ and $\text{R}_2\text{O}_2(\text{UO}_4)_2$. The authors support this view, having found that, by means of aluminium hydroxide, peruranates may be resolved into metallic peroxides and UO_4 , whilst carbonic anhydride, which has no influence on uranic acid, converts insoluble peruranates into metallic hydrogen carbonates, hydrogen peroxide, and free UO_4 ; moreover, salts have been obtained which have the formula $(\text{RO})_2\text{UO}_4$.

The sodium salt, $(\text{Na}_2\text{O}_2)\text{UO}_4$, is a yellow, crystalline powder containing $8\text{H}_2\text{O}$; dilute sulphuric, hydrochloric, acetic, and succinic acids eliminate hydrogen peroxide, whilst continuous agitation of an aqueous solution of the salt with aluminium hydroxide resolves it into peruranic acid and hydrogen peroxide, a small quantity of sodium aluminate being also produced.

The *lithium* salt, $(\text{Li}_2\text{O}_2)(\text{UO}_4)_2$, is obtained by the action of lithium hydroxide and hydrogen peroxide on uranium nitrate, being precipitated from solution by alcohol; it crystallises in short, yellow prisms containing $8\text{H}_2\text{O}$. Its behaviour towards acids and aluminium hydroxide is similar to that of the sodium salt. The *lithium* salt, $(\text{Li}_2\text{O}_2)_2\text{UO}_4$, is very unstable; it is a red, crystalline substance, which gives off oxygen in the desiccator.

The ammonium salt, $(\text{NH}_4)_2\text{O}_2(\text{UO}_4)_2$, is a bright yellow, crystalline substance containing $8\text{H}_2\text{O}$; aluminium hydroxide eliminates hydrogen peroxide. The composition of this salt indicates the existence of ammonium peroxide (compare this vol., ii, 161), which is also rendered probable by the fact that ammonia behaves towards hydrogen peroxide in the same way as the fixed alkalis; moreover, tetrethylammonium hydroxide, when agitated with an ethereal solution of hydrogen peroxide, yields an oily liquid which gives rise to hydrogen peroxide under the influence of sulphuric acid, and decomposes spontaneously at common temperatures with liberation of oxygen.

The *barium* salt, $(\text{BaO}_2)_2\text{UO}_4$, obtained from the sodium salt and barium chloride, is an orange, crystalline powder, containing $8\text{H}_2\text{O}$, and yields hydrogen peroxide with sulphuric acid; repeated treatment with carbonic anhydride yields hydrogen peroxide, peruranic acid, and hydrogen barium carbonate. The *barium* salt, $\text{BaO}_2(\text{UO}_4)_2$, is prepared from the ammonium salt and barium chloride; it is a yellow,

crystalline powder, containing $9\text{H}_2\text{O}$, and yields hydrogen peroxide when treated with sulphuric acid.

The *calcium* salt, $(\text{CaO}_2)_2\text{UO}_4$, prepared from the sodium salt and calcium chloride, crystallises in rhombic prisms, and contains $10\text{H}_2\text{O}$.

The *copper* salt, $(\text{CuO}_2)_2\text{UO}_4$, is obtained as a dark green, gelatinous precipitate on adding copper sulphate to a solution of the sodium salt.

The *nickel* salt, $(\text{NiO})_2\text{UO}_4$, separates as a greenish-yellow, gelatinous precipitate on adding nickel sulphate to a solution of the sodium salt, hydrogen peroxide being found in the filtrate.

The *lead* salt $(\text{PbO})_2\text{UO}_4 + \text{PbO}, \text{UO}_3$, a dark orange, crystalline powder, consisting of short prisms, is obtained from the sodium salt and lead acetate. Careful treatment with dilute acetic acid resolves it into lead acetate and peruranic acid without producing hydrogen peroxide.

Almost all the foregoing salts yield ozone when treated with concentrated sulphuric acid. Peroxides give rise to vigorous evolution of oxygen.

M. O. F.

Action of Carbonic Oxide on Platinum and Palladium. By E. HARBECK and GEORG LUNGE (*Zeit. anorg. Chem.*, 1898, 16, 50—66).—The method for estimating ethylene and benzene described in an earlier paper (this vol., ii, 193) is not applicable to coal-gas; this, the authors have discovered, is due to the presence of carbonic oxide, 2.6 per cent. of carbonic oxide being sufficient to prevent the action of platinum black on a mixture of ethylene and hydrogen. Moreover, if platinum black is saturated with carbonic oxide and the excess driven out with hydrogen, its action on a mixture of ethylene and hydrogen is destroyed.

Platinum black absorbs about 60 times its volume of carbonic oxide, and palladium black about 36 times its volume. The compound formed is probably a true chemical compound, since the carbonic oxide is not eliminated by the subsequent action of other gases, such as hydrogen; it is very stable, but suddenly decomposes at 250° into its constituents. The authors were unable to isolate it, as it is not volatile, and cannot be extracted by the ordinary solvents.

E. C. R.

Platinum Tellurides. By CARL ROESSLER (*Zeit. anorg. Chem.*, 1897, 15, 405—411).—*Platinum ditelluride*, PtTe_2 , is obtained by heating an intimate mixture of finely divided platinum with a slight excess of tellurium, and extracting the product with concentrated potassium hydroxide (1 water : 2 alkali) as long as tellurium dissolves. It is a grey, crystalline powder, but may be obtained in octahedra by dissolving platinum in ten times the theoretical quantity of tellurium under borax, allowing the fused mass to cool slowly, and then extracting it with cold dilute nitric acid. It is only slowly attacked by boiling concentrated nitric acid, and is not altered by boiling with concentrated potassium hydroxide, but if a rod of zinc is placed in the solution, potassium telluride is at once formed. When protected from the air, it does not melt below the boiling point of tellurium, but if

heated in the blowpipe flame, it melts to a pasty mass, which gradually loses tellurium, becomes limpid, and finally leaves a residue of platinum.

Platinum telluride, PtTe , is prepared by heating the ditelluride in the blowpipe flame until it becomes limpid, and allowing it to cool, when it crystallises out in polyhedra; good crystals may also be obtained by heating an intimate mixture of tellurium (100 grams) and platinum (150 grams) in a glass tube until combination takes place, then melting the mixture together with the glass, and dropping the hot glass into cold water. When the monotelluride is heated in the blowpipe flame for a short time, a compound is obtained which, on analysis, gives numbers approximating to those required by the formula Pt_2Te . The regulus thus obtained has a dull grey, crystalline fracture.

In analysing the above compounds, the finely powdered sample, after being fused in a platinum crucible with 10 times the quantity of a mixture of potassium nitrate (1 part) and sodium carbonate (2 parts), is extracted with water and the platinum filtered off. The solution is evaporated to dryness with hydrochloric acid, the residue dissolved in water, and the tellurium precipitated with sulphurous acid.

E. C. R.

Mineralogical Chemistry.

Copper Ore from Argentina. By JUAN VALENTIN (*Anal. Museo Nac. Buenos Aires*, 1897, 5, 28—32).—The copper ore described occurs in the Chacabuco mine, dept. Iruya, prov. Salta, along with copper pyrites, tetrahedrite, pyrites and blende in a gangue of quartz, calcite, and dolomite. It is massive with a sub-conchoidal fracture; and the colour is grey with a reddish tinge which, on exposure to the air, becomes bluish. $H = 3$; sp. gr. = 5.18—5.28. It is soluble in hydrochloric acid with evolution of hydrogen sulphide. Analysis by Kyle gave

Cu.	Fe.	Ag.	S.	CaCO ₃ .	MgCO ₃ .	Insol.	Total.
71.00	3.85	0.18	20.71	1.96	1.13	0.80	99.63.

After deducting gangue, this is interpreted as a mixture of 75.25 per cent. of copper glance (Cu_2S) and 24.56 of erubescite (Cu_3FeS_3).

L. J. S.

Cinnabar and Onofrite from Ouen-Shan-Tchiang, China. By PIERRE TERMIER (*Bull. soc. fran. min.*, 1897, 20, 204—210).—In the cinnabar mines of Ouen-Shan-Tchiang, in the province Kouei-Tchéou, Central China, the ore occurs in quartzose veins in limestone. Onofrite is present in small patches; the fracture is granular and shining and iron-black. Analyses by Pisani gave I for the cinnabar and II for the onofrite; the second agrees with the formula $(\text{Hg}, \text{Zn})(\text{S}, \text{Se})$.

	Hg.	S.	Se.	Zn, (trace of Fe).	Total.
I.	85.75	13.70	Nil	—	99.45
II.	77.3	10.3	8.4	1.3	97.3

13—2

A small quantity of onofrite, quite free from specks of enclosed cinnabar, gave 9·4 per cent. of sulphur.

The cinnabar sometimes occurs in large crystals. Interpenetrating twin crystals are described, which, in polarised light, are seen to consist of intimately intergrown right and left optically rotating individuals, the combination sometimes showing Airy's spirals. These compound crystals possess hexagonal symmetry. L. J. S.

Bauxite Deposits of Arkansas. By JOHN C. BRANNER (*J. of Geology*, 1897, 5, 263—289).—The occurrence, mining, &c., of bauxite in Arkansas are described; it is usually pisolitic, but sometimes massive in structure, and occurs in connection with syenite. Several analyses are given, the extremes are

H ₂ O.	Al ₂ O ₃ .	SiO ₂ .	Fe ₂ O ₃ .	TiO ₂ .
30·31—17·39	62·05—37·60	2·00—45·20	1·37—22·15	0—3·50

As shown by the extremes given to the right, it graduates into pisolitic kaolin. Some varieties are highly ferruginous, containing 54·9—66·85 per cent. of ferric oxide, but those which are the deepest in colour do not always contain the most iron. The various views as to the origin of bauxite are discussed, and its uses as a refractory material described. A complete bibliography is added. L. J. S.

Ankerite from Sandhurst, Victoria. By THOMAS COCKSEY (*Records Australian Museum*, 1897, 3, 63—65).—Ankerite occurs as lenticular crystals, associated with quartz, albite, and chalybite, at Sandhurst, Victoria. The surfaces of the flat rhombohedra have a yellowish tinge, but in the interior they are colourless and translucent. Analyses gave, after deducting some albite,

CaCO ₃ .	FeCO ₃ .	MgCO ₃ .	Mn.	Sp. gr.
50·76	23·97	25·93	Nil.	2·994.

This gives the formula $5\text{CaCO}_3, 2\text{FeCO}_3, 3\text{MgCO}_3$. In Boricky's general formula, $\text{CaFeC}_2\text{O}_6 + n\text{CaMgC}_2\text{O}_6$, the value of n is here 3½. L. J. S.

Langbeinite, a Tetartohedral Cubic Mineral. By OTTO LUEDECKE (*Zeit. Kryst. Min.*, 1898, 29, 255—261).—The double salt, $\text{K}_2\text{SO}_4, 2\text{MgSO}_4$, prepared artificially by Precht (*Chem. Indust.*, 1880, 3, 418) and first described as a mineral by Zuckschwerdt (*Zeit. angew. Chem.*, 1891, 356) has been found in considerable quantities at several localities (Westeregeln, Wilhelmshall, Neu-Stassfurt, Solvayhall, &c.) in the Prussian salt deposits. The mineral has a glassy lustre and a conchoidal fracture; $H = 3-4$; sp. gr. = 2·83. It is slowly decomposed by water, and attracts moisture from the air. Analyses by Zuckschwerdt of grey and white material gave I and II respectively; III, by Wagner, is of transparent material.

	K ₂ SO ₄ .	MgSO ₄ .	CaSO ₄ .	MgCl ₂ .	MgO.	NaCl.	H ₂ O.	Sp. gr.
I.	41·30	58·20	—	0·22	0·08	—	—	} 2·86
II.	38·99	58·55	0·50	0·55	0·13	0·43	0·78	
III.	41·0	58·1	—	—	—	—	1·0	

The cubic crystals are very rare; they are of interest in being tetartohedral (tetrahedral-pentagonaldodecahedral class of Groth). One crystal shows the forms, {100}, {111}, { $\bar{1}\bar{1}\bar{1}$ }, {2 $\bar{1}$ 1}, {2 $\bar{2}$ 1}, {310}, {210}, {920} and {110}; the arrangement of the faces is as on the crystals of sodium chlorate which rotate the plane of polarisation to the left. The crystals of langbeinite are optically inactive; index of refraction for sodium light, 1.5281; for thallium light, 1.5343.

L. J. S.

Planoferrite. By L. DARAPSKY (*Zeit. Kryst. Min.*, 1898, 29, 213—216).—The name planoferrite is given to a new hydrated basic ferric sulphate occurring with copiapite, coquimbite, and other sulphates in the "Lautaro" copper mine at Morro Moreno, near Antofagasta, Chili. The small tabular crystals are determined by F. Grünling to be probably orthorhombic; they are yellowish-green to brown in colour, and have a perfect cleavage parallel to the large plane. Water easily decomposes the mineral with separation of basic ferric sulphate. Analysis gave

Fe ₂ O ₃ .	SO ₃ .	H ₂ O.	Insol.	Total.
31.20	15.57	51.82	1.41	100.00

corresponding with Fe₂O₃.SO₃.15H₂O. This is more basic than amarantite, and contains more water than other basic ferric sulphates. It may have been formed by the alteration of copiapite.

Analyses are also given of material from the salt deposits near Taltal, Chili, consisting of mixtures of glauberite, blödite, soda nitre, and rock salt.

L. J. S.

Beresowite, a New Mineral. By J. SAMOILOFF (*Bull. Soc. Imp. des Naturalistes Moscow*, 1897, 290—291).—Beresowite occurs with galena and cerussite at Beresowsk in the Urals. The indistinct tabular crystals are dark red, and resemble melanochroite; they have a perfect cleavage in one direction and are pleochroic; sp. gr. = 6.69. Pseudomorphs of beresowite after crocoite are also found. Analysis gave results agreeing with the formula 2PbO, 3PbCrO₄, PbCO₃.

PbO.	CrO ₃ .	CO ₂ .	Total.
79.30	17.93	2.46	99.69

L. J. S.

Gedrite-schist from Dalecarlia. By MATS WEIBULL (*Jahrb. f. Min.*, 1897, ii, Ref. 443—445; from *Geol. För. i Stockholm Förh.*, 1896, 18, 377).—Amongst the quartz-hornblende-schists occurring in the mining district of Vester-Silfberg, in southern Dalecarlia, is a variety containing the orthorhombic aluminous amphibole, gedrite. Besides much quartz and bundles of gedrite, this contains some orthoclase, magnetite, apatite, and albite. The gedrite individuals are 2—3 cm. long and 0.5 mm. thick. Detailed optical determinations are given; the pleochroism is strong. Gedrite of sp. gr. = 3.243 gave, on analysis by J. Petré, n,

SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
47.40	13.68	23.38	2.36	7.32	3.21	trace	1.97	99.32

Formula: $10R''SiO_3 + 2R'Al_2SiO_6 + R'Al(SiO_3)_2$, where $R' = H + Na$, and $(Fe + Mn) : Mg : H_2 : Na_2 = 6 : 3 : 2 : 1$.

The mineral, in containing alkali, approaches to glaucophane in composition.

L. J. S.

Hornblende-Basalt from Mitlechtern. By K. VON KRAATZ-KOSCHLAU (*Jahrb. f. Min.*, 1897, ii, Ref., 475—476; from *Notizbl. Ver. f. Erdkunde Darmstadt*, 1896, [iv], 17, 23—28).—Hornblende-nepheline-basalt from the central portion of a dyke, 6—8 m. thick, gave analysis I; towards the margins of the dyke, iron ore becomes more plentiful, and hornblende and nepheline are replaced by biotite and plagioclase respectively. Anal. II is of the hornblende-granite which is cut by the basalt dyke; it contains orthoclase, plagioclase, biotite, hornblende, and titanite. Altered granite from near the basalt-contact gave anal. III. The high percentage of water in I and III is considered to represent the water originally contained in the basaltic magma.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	Total
I.	40.19	not det.	11.91	6.24	6.63	trace	12.67	13.13	2.90	2.34	4.19	100.20
II.	61.33	„	16.12	3.34	3.00	„	5.73	5.45	2.32	3.27	0.85	101.41
III.	58.44	„	16.77	3.67	2.75	„	4.63	4.64	2.62	4.35	3.02	100.89

L. J. S.

The Monchiquites or Analcite Group of Igneous Rocks. By LOUIS V. PIRSSON (*J. of Geology*, 1896, 4, 678—690).—That a basic rock like monchiquite, occurring in deep-seated dykes, should contain so much glass is rather anomalous. Hunter's analysis of the so-called glassy base of the original Brazilian monchiquites (Abstr., 1892, 1058) gives the molecular ratios, $SiO_2 : Al_2O_3 : Na_2O : H_2O = 4 : 1 : 1 : 2$, as in analcite. This glassy base has, then, the exact chemical composition, the exact specific gravity, the property of gelatinising with acids, and the optical properties of analcite; it must therefore be that mineral, and not a pitchstone glass as was formerly supposed.

This analcite is of primary origin, as in the analcite-basalt from Montana described by Lindgren (Abstr., 1892, 1413), and as there is a leucite group of rocks, so is there an analcite group. The analcite-basalts corresponding with the leucite-basalts are the monchiquites of Rosenbusch, and the analcites, or olivine-free analcite-basalts, are the fourchites of J. F. Williams.

L. J. S.

Analcite-basalt from Colorado. By WHITMAN CROSS (*J. of Geology*, 1897, 5, 684—693. Compare preceding abstract).—A black basaltic rock occurs, presumably as a dyke, at "The Basin," west of Cripple Creek, in Colorado. Besides phenocrysts of augite, olivine, and analcite, there are also present feldspars, magnetite, biotite, and apatite. The analcite, which occurs as white isotropic grains, gave analysis I; the silica is somewhat low, but there is no reason for doubting the reference to analcite. The portion of the rock soluble in hydrochloric acid has practically the same composition. The pale yellow augite gave the results under II. The bulk analysis of

the rock is given under III. The analyses are by W. F. Hillebrand.

	SiO ₂ .	ZrO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	SrO.	BaO.
I.	51.24	—	—	24.00	1.20	—	—	1.62	0.06	—
II.	49.26	—	1.53	6.07	3.31	4.23	—	21.79	0.06	?
III.	45.59	0.03	1.32	12.98	4.57	4.70	0.14	11.09	0.12	0.13

	MgO.	K ₂ O.	Na ₂ O.	Li ₂ O.	(over H ₂ SO ₄).	H ₂ O. (remainder).	SO ₃ .	Cl.	P ₂ O ₅ .	Total.
I.	0.33	1.25	11.61	—	0.62	8.47	Nil	trace	—	100.40
II.	12.40	0.41	0.79	—	—	—	—	—	—	99.79
III.	8.36	1.04	4.53	trace	0.51	3.40	—	0.05	0.91	99.87

The plagioclase-basalts of the same region have the same composition but with less water, the presence of which has influenced the formation of analcite. L. J. S.

Contact Metamorphism of Phyllites. By K. DALMER (*Jahrb. f. Min.*, 1897, ii, 215—218. Compare this vol., ii, 82).—The green mineral of phyllites, which is decomposed by hydrochloric acid, is considered to be probably thuringite. This consists, according to Rammelsberg, of mixtures, in varying proportions, of $2(\text{Al,Fe})_2\text{O}_3 \cdot \text{SiO}_2$ and $2(\text{Fe,Mg})\text{O} \cdot \text{SiO}_2$ with water; and, after deducting muscovite, the results of some analyses are made to agree with this formula. According to Tschermak, biotite also contains the olivine molecule $2(\text{Fe,Mg})\text{O} \cdot \text{SiO}_2$.

These formulæ are used in an equation (which is a modification of that given in the previous paper) to express the change from a phyllite, consisting of muscovite, quartz, and thuringite, to a rock containing biotite and andalusite. Cordierite could also be produced from a mixture of muscovite, quartz, and thuringite. L. J. S.

Average Specific Gravity of Meteorites. By OLIVER C. FARRINGTON (*J. of Geology*, 1897, 5, 126—130).—From the weights and specific gravities of 142 meteorites of which the fall has been recorded during the last hundred years, the average specific gravity of meteoric matter is deduced as being 3.69. L. J. S.

Meteoric Iron from Beaconsfield, Australia. By EMIL W. COHEN (*Sitz.-ber. Akad. Berlin*, 1897, 1035—1050).—This iron, which has recently been found near Beaconsfield, Mornington Co., Victoria, originally measured $30 \times 30 \times 15$ cm., and after a portion of the thick coating of rust had been removed, it weighed 75 kilos.; it exudes much ferrous chloride, and is consequently liable to rapid alteration. It is an octahedral iron of coarse structure with kamacite predominating. Crystals of schreibersite gave analysis I, agreeing with the ratio $(\text{Fe,Ni,Co}) : \text{P} = 3.1585 : 1$. Fine needles of rhadbite gave II, here $(\text{Fe,Ni,Co}) : \text{P} = 3.0533 : 1$. The tænite gave III after deducting some nickel-iron phosphide. Indistinct crystals of cohenite are of irregular distribution in the iron; after deducting a little schreibersite, which closely resembles cohenite in physical characters, it gave the results under IV; $(\text{Fe,Ni,Co}) : \text{C} = 3.064 : 1$. Nodules of troilite gave V;

(Fe,Ni,Co) : S = 1 : 0.9901. Graphite, carbonaceous matter, and silicate grains are also present. The bulk analysis of the iron gave VI; this corresponds with 98.07 per cent. of nickel-iron.

	Fe.	Ni.	Co.	Cu.	C.	P.	S.	Cl.	Total.	Sp. gr.
I.	66.92	18.16	0.62	—	—	14.88	—	—	100.58	7.17
II.	[41.54]	42.61	[0.80]	—	—	15.05	—	—	100.00	—
III.	[50.92]	47.98	0.63	—	0.47	—	—	—	100.00	7.1297
IV.	90.94	2.22	0.30	—	6.54	—	—	—	100.00	7.2014
V.	58.07	4.34	1.52	—	—	trace	36.07	trace	100.00	4.7379
VI.	92.56	7.34	0.48	0.02	0.05	0.26	0.04	0.01	100.76	—

In the rust is a substance with the characters of stilpnosiderite (limonite); it contains a little nickel and cobalt. This iron is possibly part of the same fall as the Cranbourne iron (Abstr., 1883, 169).

L. J. S.

The Nocoleche Meteorite. By THOMAS COOKSEY (*Records Australian Museum*, 1897, 3, 51—62).—This iron, which was found in 1895 near Nocoleche Station, Wanaaring, N.S. Wales, weighed 20,048 grams, and measured $12\frac{3}{4} \times 11\frac{1}{2} \times 5\frac{1}{2}$ cm. It is an octahedral iron with broad bands of kamacite. The mean of four partial analyses of material visibly free from troilite is given under I, sp. gr. = 7.721, 7.796.

	Fe.	Ni.	Co.	Cu.	P.	S.	Residue.	Total.
I.	96.93	2.91	0.21	0.05	0.12	0.11	0.08	100.41
II.	62.01	0.89		—	—	38.28	trace	101.18

Troilite nodules are freely distributed; sp. gr. = 5.50, 5.442. After extracting, by the prolonged action of a solution of mercuric chloride, 34.6 per cent. of intimately intermixed metallic iron, the troilite gave analysis II; sp. gr. = 4.645.

A catalogue and bibliography of all the known Australian meteorites is added.

L. J. S.

The Fisher Meteorite. By NEWTON H. WINCHELL (*Amer. Geologist*, 1897, 20, 316—318).—This stone fell on April 9th, 1894, at Fisher, Polk Co., Minnesota; the smaller of the two fragments weighs about $9\frac{1}{2}$ pounds (*ibid.*, 1894, 14, 389). It consists mainly of olivine and enstatite with occasionally chondritic structure; there are specks of metallic iron and troilite; and glassy matter, asmanite (tridymite), and maskelynite are also perhaps present (*ibid.*, 1896, 17, 173, 234; and *Compt. rend.*, 1896, 122, 681). In the present paper, the somewhat slender evidence for the presence of maskelynite is recapitulated. Analysis of the meteorite by C. P. Berkey gave:

SiO ₂ .	Al ₂ O ₃ .	Fe.	MgO.	CaO.	Ni.	S.	Total.	Sp. gr.
41.16	6.60	24.26	19.03	4.34	2.26	trace	97.65	3.44

The iron shown above exists in the native state and also as silicate, oxide, and sulphide.

L. J. S.

Physiological Chemistry.

Active Absorption of Oxygen by the Lungs. By J. LORRAIN SMITH (*J. Physiol.*, 1898, 22, 307—318).—Various pathological conditions (fever, toxic agents of bacterial origin, local changes in the lung produced by high pressure oxygen) interfere with the active absorption of oxygen by the pulmonary epithelium, and reduce the oxygen tension of the arterial blood to about that of the alveolar air.
W. D. H.

Effect of Division of the Food into Several Meals on Proteid Katabolism. By OTTO KRUMMACHER (*Zeit. Biol.*, 1897, 35, 481—505).—The research was carried out for prolonged periods, and numerous observations were made during that time. There is an increase in the discharge of nitrogen if the day's food is given in one large meal; estimation of the ethereal hydrogen sulphates in the urine shows, however, that the difference is due to variations in the putrefaction of proteid in the intestines, and not to an alteration in true metabolic processes.
W. D. H.

The Action of Superheated Water on Proteids. By ERNST L. SALKOWSKI (*Zeit. Biol.*, 1897, 34, *Jubelband*, 190—245).—Muscle and fibrin were employed, the latter being more soluble in superheated water than muscle, of which, as a rule, more than half is left undissolved. The atmid-albumoses so formed are described, and points of difference from Neumeister noted. Feeding experiments with the product are given, but are at present incomplete, the principal point made out being that much proteid matter is unused, the presence of the atmid-products apparently stimulating putrefactive processes in the intestine.
W. D. H.

Physiology of the Salmon in Fresh Water. By D. NOËL PATON, FRANCIS D. BOYD, JAMES C. DUNLOP, A. LOCKHART GILLESPIE, G. LOVELL GULLAND, E. D. W. GREIG, and M. I. NEWBIGIN (*J. Physiol.*, 1898, 22, 333—356).—Salmon apparently do not feed while in fresh water; this is shown by an examination of the alimentary tract, and by the low proteolytic activity of its glands; there is increase in the putrefactive organisms, which is probably due to the diminished activity of the stomach contents.

The metabolism in the salmon under these circumstances was studied by observations on the changes in the solids of muscles, ovaries and testes, and in the fats and proteids of these and other organs. The observations are histological and chemical, and numerous analytical details are given. The proteids in muscle described are paramyosinogen, myosinogen, myoglobulin, and a small amount of nucleo-proteid. Some of the proteid is not soluble in saline solution, but is soluble in 1 per cent. sodium hydroxide. The soluble proteids diminish in the upper waters of the river.

If from the fat and proteid lost from the muscles the amount going to the ovaries and testes be subtracted, the residue gives the amounts

available for the liberation of energy. Up to August, the ratio of the energy from proteids to that from fats is 1 : 4·2, and to November, the proportion is 1 : 7·6 in female fish ; up to August, 1 : 11·6 in male fish. With regard to phosphorus, the results indicate that the phosphorus stored in the muscles as phosphates is transferred to the generative organs and is there built up into organic combinations. In both ovary and testes, lecithin is an important step in this conversion, and in the ovary, ichthulin, a pseudo-nuclein, is an intermediate step to the true nucleins ; this stage is absent in the testes.

The increase of iron in the ovaries is not derived from muscle, but from the hæmoglobin of the blood.

The colour of salmon flesh and ovary is due to two lipochromes, yellow and red. The yellow pigment is probably derived from the herring, &c., on which the salmon feeds, whilst the red pigment is possibly formed from the yellow ; as the season advances, the red pigment disappears from the muscles and accumulates in the ovaries.

W. D. H.

Applications of Dialysis to certain Questions in Chemical Physiology. By MAURICE ARTHUS (*Zeit. Biol.*, 1897, 34, *Jubelband* 432—446).—The method of dialysis is regarded as a valuable one, and its use is described in connection with the questions of the importance of calcium salts in blood coagulation, of the state of sugar in the blood, and in the preparation of oxyhæmoglobin crystals. In connection with the first of these points, new experiments are described which confirm the author's previous work, and are opposed to the views of A. Schmidt. The sugar of the blood behaves as if it were free there ; glycolysis can be avoided by a low temperature or by the addition of 1 per cent. of sodium fluoride.

The addition of alcohol to an aqueous solution of oxyhæmoglobin causes crystallisation of this substance. This method may be most successfully carried out by placing the solution in a dialyser plunged in dilute alcohol.

W. D. H.

Non-coagulable Proteids of Muscle. By KARL MAYS (*Zeit. Biol.*, 1897, 34, *Jubelband*, 268—297).—The research relates to the presence in muscle of proteid material which is not coagulated by heat. Opinions are divided on the question as to whether fresh muscle contains proteoses ; the present work shows that there is some proteid material which is not coagulated by heat. A considerable section of the paper is devoted to the occurrence of nucleon (phosphocarnic acid) in muscle and in meat extracts, Siegfried's statements being, on the whole, confirmed ; this substance, however, is completely precipitated by saturation with ammonium sulphate, and cannot therefore be classed with the peptones.

W. D. H.

A Method of Freeing Flesh from Fat. By OTTO FRANK (*Zeit. Biol.*, 1897, 35, 549—554).—The objection to Dormeyer's digestion method of obtaining the fat from muscle is that the lecithin undergoes decomposition, and the proteid material is so changed that further investigation of it is impossible.

The present research shows that an almost complete extraction of

the fat from finely divided flesh can be accomplished by extraction with 96 per cent. alcohol followed by extraction with ether for 24 hours in a Soxhlet extractor. (Compare Bogdanow, this vol., ii, 84.)

W. D. H.

Extraction of Fat. By ERWIN VOIT [and OTTO KRUMMACHER] (*Zeit. Biol.*, 1897, 35, 555—582).—This, like Frank's researches (preceding abstract), is work which shows that Dormeyer's method has many disadvantages. If small quantities of material as free from water as possible are taken, and the extraction with ether properly carried out, all the fat can be generally obtained in the extract; certainly 95 per cent. of the fat is always removed. Some sources of error, however, in the extraction have still to be explained.

W. D. H.

Composition of Human Milk. By ALFRED H. CARTER and H. DROOP RICHMOND (*Brit. Med. J.*, 1898, i, 199—203).—A large number of analyses are given. The proteids, ash, and sugar decrease as lactation advances, the composition of the fat (as indicated by the refractive index) also varies, the amount of the volatile acids increasing as lactation proceeds.

Milks which disagree with infants are generally those in the early stage; probably here the normal functions of the breast are delayed and the colostrum period prolonged.

W. D. H.

Relations between the Growth of the Offspring and the Composition of the Milk in various Mammals. By FR. PRÖSCHER (*Zeit. physiol. Chem.*, 1897, 24, 285—302).—The variations in the composition of the milk in different animals suggests that this is explicable, from the teleological standpoint, on the different stages at which birth takes place, some constituents being more suitable at certain stages of growth than others. This is confirmed by comparing the most trustworthy of the analyses of milk hitherto published. The difference in the needs of the suckling offspring and the adult may be thus summarised: the infant needs more proteid for tissue formation, more fat for heat production because it has a relatively large surface area, and less carbohydrate because it does less work.

W. D. H.

Secretion of the so-called Salivary Glands of Octopus macropus. By IDA H. HYDE (*Zeit. Biol.*, 1897, 35, 459—477).—The secretion obtained by electrical stimulation contains proteid, but mucin is absent; the action of the juice is not described.

W. D. H.

The Excretion of Ammonia and Ammonium Salts by the Human and Animal Body. By THEODOR RUMPF, and G. KLEINE (*Zeit. Biol.*, 1897, 34, *Jubelband*, 65—124).—Large doses of organic ammonium salts are not oxidised in the body, but increase the excretion of ammonia; with ammonium formate, the volatile acids of the urine are also increased. The ammonia leaves the body mostly as chloride, less as the sulphate, and least as the phosphate. The increase in the acid components is, however, greater than that of the ammonia. The excretion of urea is lessened.

Of the salts used, ammonium carbonate is most easily oxidised; formate, acetate, and citrate follow in the order named.

Sodium phosphate and calcium carbonate cause a small decrease in the excretion of ammonia, but magnesium phosphate has no effect. The alkali salts of organic acids lessen the ammonia considerably. The inorganic ammonium salts undergo decomposition into organic combinations, which increase the alkalinity of the blood, and, in the case of ammonium carbonate, powerful toxic effects are observed; it is probable that this organic compound is ammonium albuminate.

W. D. H.

Action of Distilled Water on Tubifex. By SYDNEY RINGER (*Proc. physiol. Soc.*, 1897—8, 14. Compare Abstr., 1895, ii, 39).—The experiments recorded confirm Locke's conclusion that copper in even infinitesimal quantities will disintegrate *Tubifex*, whilst water free from copper and other heavy metals, and without any salts, such as calcium salts, can sustain the life of the animal.

W. D. H.

Physiological Action and Chemical Constitution of Piperidine, Coniine, and Nicotine. By B. MOORE and R. ROW (*J. Physiol.*, 1398, 22, 273—295).—The alkaloids mentioned are similar in physiological action, and they all contain a reduced pyridine (or pyrroline) ring. Intensification of the action is due to the introduction of an organic radicle as a side group.

Motor paralysis (in frogs) is due to an effect on the intramuscular part of the motor nerves; the excised heart is slowed and the systole prolonged. The heart *in situ* in mammals is at first slowed. The arterial blood-pressure is raised, owing to constriction of the arterioles, this being probably due to vaso-motor excitation in peripheral ganglia; at a certain stage, this mechanism is paralysed, further administration of the drugs no longer affecting blood-pressure.

W. D. H.

Physiological Effects of Extracts of Supra-renal Capsules. By SWALE VINCENT (*J. Physiol.*, 1898, 22, 270—272. Compare Abstr., 1897, ii, 420, 573).—In dogs and cats, subcutaneous injection of large doses of extracts of supra-renal capsules is fatal, the symptoms observed being similar to those already described in other animals. With the possible exception of the thyroid, the supra-renal appears to be the only mammalian tissue or organ which produces toxic effects when a boiled and filtered extract is administered subcutaneously.

W. D. H.

The Biuret Reaction in Human Urine. By H. BAREND J. STOKVIS (*Zeit. Biol.*, 1897, 34, *Jubelband*, 466—470).—In cases where peptonuria is suspected, the positive results of the biuret reaction, and of precipitation by phosphotungstic acid or ammonium sulphate cannot be depended on in the presence of urobilin, which responds to all these reactions.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation Phenomena. By ALFRED STAVENHAGEN (*Ber.*, 1897, 30, 2963).—A reply to Buchner and Rapp (this vol., ii, 127). The author states that his extract was capable of fermenting before it was filtered, and also points out that he used a Kitasato filter, and not a Chamberland.
J. J. S.

Zymase. By RICHARD NEUMEISTER (*Ber.*, 1897, 30, 2963—2966. Compare Buchner, *Abstr.*, 1897, ii, 154, 380; this vol., ii, 127).—The author considers that the active principle of Buchner's extract is not an enzyme (zymase), but is more probably a mixture of complex proteids whose interactions bring about the fermentation. The author compares Buchner's results with those obtained by Kühne with extract of frog's muscles. Buchner's view of the existence of two enzymes in the same cell, one of which can completely destroy the other, is held to be untenable.
J. J. S.

Alcoholic Fermentation without the aid of Living Yeast Cells. By MARIE VON MANASSEIN (*Ber.*, 1897, 30, 3061—3062. Compare Buchner, *Abstr.*, 1897, ii, 154, 380; Stavenagen, this vol., ii, 88, and Neumeister, preceding abstract).—The author states that, as early as 1871, she pointed out that living yeast cells are not necessary for alcoholic fermentation, and that the fermentation is to be regarded as a chemical process brought about by an enzyme formed in the yeast.
J. J. S.

Denitrification. By G. AMPOLA and E. GARINO (*Gazzetta*, 1897, 27, ii, 197—206).—It is shown that a denitrifying organism isolated by the authors, the *Bacterium denitrificans agilis*, when cultivated at 35—36° in nitrated broth, causes the evolution of nitrogen containing 15 per cent. of carbonic anhydride.
W. J. P.

Maturation of Fruits. By MAXIMILIEN GERBER (*Ann. Agron.*, 1897, 23, 606—607; from *Ann. Sci. Nat.*, [viii], *Botan.*, 4, 1).—When fruits containing malic, citric, or tartaric acid, such as apples, pippins, or grapes, are kept at 30°, the respiratory quotient, CO_2/O_2 , which is at first more than 1, decreases until it becomes 1 or even less. It is concluded that the acids are progressively consumed with liberation of carbonic anhydride; a carbohydrate is, at the same time, formed. When *Sterigmatocystis Nigra* is cultivated in Raulin's liquid, containing malic, citric or tartaric acid instead of saccharose, the carbohydrate, callose, is produced under the form of the mycelium, and the respiratory quotient is high.

In the case of fruits containing tannin, the respiratory quotient is below 1, whilst *S. Nigra* cultivated in Raulin's liquid (with tannin as the only source of carbon) produces carbohydrates, and has a respiratory quotient higher than 1. With fruits, the tannin is probably destroyed without production of carbohydrates; ethers are then

formed, producing a higher respiratory quotient. It is suggested that at this period the insoluble pectose of the cell-wall is transformed into soluble pectin, causing respiration to be obstructed, with the result that the fruit is forced to depend on the fermentation of its saccharine matter to enable it to obtain the necessary energy to live. The fermentation resembles those observed by Lechartier and Bellamy in fruits in a confined atmosphere.

The original paper contains a very complete bibliography on the subject of the maturation of fruits. N. H. J. M.

Composition of the Mycelia of Moulds. By MARSCHALL (*Chem. Centr.*, 1897, i, 115—116; from *Arch. Hyg.*, 28, 16—29).—Cultures of *Aspergillus niger*, *Penicillium glaucum*, and *Mucor Stolonifer* were made in peptone-meat extract containing 1 per cent. of tartaric acid and 2 per cent. of dextrose; the albuminous and non-albuminous nitrogenous substances were separated by ferric acetate. Taking the mean, it was found that the mycelia of these moulds contain 38 per cent. of albumin, 5.27 of substances soluble in ether, 14.03 of substances soluble in alcohol, 6.37 of ash, 5.03 of cellulose, 2.80 of starch, and 28.47 of nitrogenous substances soluble in water. Bacteria, even when cultivated in material rich in sugar, contain more nitrogenous substances than the moulds, but at the most only traces of cellulose and starch. The spores of the moulds contain twice as much cellulose, starch, and substances soluble in alcohol as the mycelia, but are poorer in albumin. As regards composition, the moulds occupy a position intermediate between fungi and bacteria; they are richer in nitrogen than the former, but poorer in carbohydrates. E. W. W.

Influence of Oxygen and other Substances on the Formation of Chlorophyll. By WLADIMIR PALLADIN (*Compt. rend.*, 1897, 125, 827—829).—Etiolated leaves, almost free from carbohydrates, were floated on recently boiled water and on aqueous solutions of various substances and exposed to light, the formation of chlorophyll being noted. Certain substances, such as saccharose, raffinose, dextrose, levulose, maltose, glycerol, galactose, lactose, and dextrin assist in the production of chlorophyll, whilst others, such as inulin and tyrosin, have no action, and a third group, including mannitol, dulcitol, asparagine, carbamide, alcohol, ammonium chloride, and quinic acid retard or prevent its formation. If one of the leaves falls to the bottom of the liquid, no chlorophyll is formed in it. Direct experiments showed that the formation of the chlorophyll in etiolated leaves only takes place when oxygen is present, and the author concludes that it is essential to the production of the chlorophyll that the vegetable tissues receive more oxygen than is necessary for their respiration. C. H. B.

Vegetable Lecithin. By ERNST SCHULZE (*Chem. Zeit.*, 1897, 21, 374—376).—This paper is merely a *résumé* of work previously published, both by the author and others. (Compare Abstr., 1891, 413, 489, and 511; 1894, ii, 155 and 402; 1895, ii, 96). A method is given for the estimation of the amount of lecithin present in different vegetable tissues, depending on the estimation of phosphorus in the

ethereal and alcoholic extracts. The author points out that the method is not very accurate, since different lecithins (dipalmityllecithin, distearyllecithin and dioleylecithin) contain different percentages of phosphorus. The amounts of lecithin usually present in different seeds are given, and also the distribution of the lecithin within the seed. Attention is also drawn to the relationship between lecithin and chlorophyll. The author states that, in giving the amount of fatty material in foods (oil cakes, &c.), the lecithin should always be included, as on digestion it becomes converted into fatty acids, choline, and glycerophosphoric acid.

J. J. S.

Formation of Albumin in Phanerogamic Plants. By BARTHOLOMEW HANSTEEN (*Chem. Centr.*, 1897, i, 295; from *Ber. Deut. bot. Ges.*, 14, 362—371).—Kinoshita studied the formation of albumin from asparagine in leguminous plants by allowing young roots, from which the cotyledons had been removed, to grow in 1 per cent. solutions of methylic alcohol and of glycerol. The author points out that the experimental conditions of growth were widely different from those which obtain when the plants grow naturally, by assimilation of the inorganic salts of the soil; experiments were, therefore, made with pure cultures of the aquatic plant *Lemna minor*, which normally assimilates organic material from aqueous solution. The culture media were solutions of dextrose and of cane-sugar, containing a nitrogenous substance; asparagine, carbamide, glycocine, leucine, alanine, potassium and sodium nitrates, and the chloride and sulphate of ammonium were employed. The cultures were kept in darkness three or four days before use, and thus rendered free from starch; the temperature throughout the experiments being 20°. It was found that when no light was admitted, the plant converted sugar into starch, and absorbed asparagine; hence, when the absorption of the sugar and asparagine occurred simultaneously, and no starch, or traces only, were found in the plant, the author concluded that the sugar had been transformed into albumin. In the presence of asparagine, starch was formed from cane-sugar, whilst none was obtained from dextrose; thus, whilst the plant fails to elaborate albumin from cane-sugar, it is successful in doing so from dextrose. This explains the fact that, in young potato-shoots, asparagine and cane-sugar exist together. Albumin was formed from both cane-sugar and dextrose in the presence of carbamide; from cane-sugar only, when glycocine was employed; and from neither dextrose nor cane-sugar when leucine, creatine, alanine, or the nitrates were present. The ammonium salts gave the same results as asparagine. When albumin is formed from asparagine alone, the presence of potassium or sodium chloride greatly influences the result, and it is probable that the presence of these chlorides is an important factor in plant-growth.

W. A. D.

Decomposition Products of the Proteids of Conifer Seeds. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1897, 24, 276—284. Compare *Abstr.*, 1897, ii, 156).—The proteid materials were extracted from *Picea excelsa* by Ritthausen's method, and heated with hydrochloric acid and stannous chloride. Arginine was separated out from the filtrate in large quantities, 100 parts of proteid yielding as much

as 10 parts of arginine. In Hedin's researches, the quantity of arginine he obtained from various proteids amounted to 0.25—2.75 per cent. Of the precipitate produced by phosphotungstic acid, two-thirds consisted of arginine, whilst leucine and tyrosine were found in the filtrate. Similar results were obtained with the proteid matter from *Abies pectinata*.

Kossel considers that, on the hydrolysis of protamine, 3 molecules of arginine, 1 of histidine, and 1 of lysine are obtained. The large yield of arginine in the present research suggests that it originates from a protamine nucleus.

W. D. H.

Source of Allylthiocarbimide in the Root of Cochlearia Armoracia. By JOHANNES GADAMER (*Arch. Pharm.*, 1897, 235, 577—581. Compare Abstr., 1897, i, 360).—Alcohol extracts a considerable amount of cane-sugar from the dried and pulverised roots of *Cochlearia Armoracia* (horse-radish); the aqueous extract is bitter, but from it no glucoside could be directly isolated, although its presence is proved by the following experiments.

The united extracts are evaporated, treated with silver nitrate, and the resulting precipitate treated with ammonia, when a silver ammonium compound is produced, identical with the substance obtained in a similar manner from sinigrin, so that, in all probability, the glucoside contains myronic acid (as the potassium salt).

Apparently, in all plants which give allylthiocarbimide on hydrolysis, myronic acid, that is, sinigrin, must be looked on as the source of the thiocarbimide; this point is being further investigated.

A. W. C.

Some Comparatively Rare Constituents of the Carbonised Vinasse of a Beet-Sugar Factory. By EDMUND O. VON LIPPMANN (*Ber.*, 1897, 30, 3037—3039).—In the course of attempts to refine the carbonised vinasse from a factory in which the recovery of sugar from beetroot molasses is carried out, the author obtained certain muddy residues; these were found to contain 0.03 per cent. of lithium, 0.12 per cent. of titanium, and 0.243 per cent. of manganese, calculated on the dry substance.

Beets that had been manured with chalk mud containing strontium contained 0.21 part per thousand of strontia; the amount of lime commonly present is 0.4—0.5 part. Hay from some red clover which had grown on a heap of strontium residues contained 13.2 parts of strontia per thousand; the usual amount of lime is 20—24 parts. Employment in the sheds where the strontium salts are manipulated has been found to bring on temporary eczema in workmen predisposed to that disease.

C. F. B.

Composition of the Ash of Canary Seed. By T. S. HOFMAN (*Landbouwkund. Tijdschr.*, 1897, 5, 172—173).—The air-dried seed of *Phalaris canariensis*, grown at Wageningen, contained 3.26 per cent. of pure ash (free from sand and carbon) of the following percentage composition.

K ₂ O.	Na ₂ O.	CaO.	MgO ₁	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
5.3	0.3	1.6	3.9	1.8	22.8	12.9	51.7	1.9

N. H. J. M.

Ash of Gidgea Acacia (Stinking Wattle). By FREDERICK B. GUTHRIE (*Agric. Gaz. New South Wales*, 1897, 8, 868—869).—The pure ash (excluding sand, carbon, and carbonic anhydride) of *Gidgea Acacia* was found to have the following percentage composition.

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	SiO ₂ .	P ₂ O ₅ .	SO ₃ .	Cl.
0.60	0.72	90.71	2.74	1.17			1.47	1.72	0.04

The wood of *Gidgea*, both green and dry, burns completely when once alight, leaving a white ash, which is used for polishing, &c. The wood is excessively hard and very durable. The dry substance of the leaves contains 26.92 per cent. of proteids. N. H. J. M.

Amount and Composition of the Herbage of Meadows at different Periods. By F. VILLARD and F. BEUF (*Ann. Agron.*, 1897, 23, 497—527).—The experiments were made (1) on a natural meadow, (2) with lucerne, growing on a poor soil, with 30 per cent. of other herbage, mostly coarse grass, and (3) with a mixture of sainfoin (70 per cent.), lucerne (21 per cent.) and miscellaneous herbage. Samples were taken at intervals of a week, commencing May 8 or 14, and the dry matter and the different constituents determined. From the fourth week, the amounts of total produce were also determined. The condition of the crops at the various dates were as follows (the numbers refer to the three experiments):—May 29 (1 and 3), first flowers; June 4, (1) *Leguminosæ* in flower, (2) first flowers; June 11, (1) grasses in flower, (3) in flower; June 18, (1) *Leguminosæ* forming fruit, (3) end of flowering; June 25, (1 and 3) all fruit formed, (2) end of

	Fresh produce.	Dry produce.	Proteid.	Ether extract.	N-free extract.	Cellulose.	Ash.	P ₂ O ₅ .	Nutritive ratio.
<i>Natural Meadow.</i>									
29 May ...	30460	6870	1150	158	3557	1334	673	46	3.22
4 June ...	32520	8050	1228	217	4076	1805	725	43	3.49
11 „ ...	28160	7180	1045	194	3646	1666	629	39	3.67
18 „ ...	34210	10110	1370	334	5215	2374	817	47	4.04
25 „ ...	24760	9032	1061	271	4465	2439	796	55	4.46
<i>Lucerne.</i>									
4 June ...	26540	6370	903	153	2966	1697	661	25	3.44
11 „ ...	24370	6180	981	105	2858	1706	529	21	3.02
18 „ ...	22050	5515	900	121	2515	1561	418	18	2.93
25 „ ...	19870	5345	802	139	2242	1769	393	19	2.97
2 July ...	21590	7100	936	206	2898	2499	561	24	3.31
<i>Sainfoin and Lucerne.</i>									
29 May ...	25590	4856	822	126	2532	977	398	24	3.23
4 June ...	25730	5403	928	135	2508	1463	368	26	2.84
11 „ ...	24920	5906	999	166	2729	1677	359	30	2.87
18 „ ...	24770	6242	1069	131	2497	1991	554	22	2.45
25 „ ...	17390	5095	799	143	2168	1667	319	22	2.89

flowering ; July 2, (2) fruit. The summary on p. 181 shows the amounts of fresh and dry produce, and constituents in kilograms per hectare.

The percentage results are also given in tables, and the amounts per hectare are shown in curves in the original.

It is concluded that in deciding as to the best time for cutting, two things must be considered, the amounts of nutritive constituents in the crop, and the determination of the plants as the season advances. In the case of the mixed herbage of meadows, (1) and the mixture of sainfoin and lucerne, (2) the most favourable time was shown to be the period of full flower. As regards lucerne (2) which begins to deteriorate earlier, the best time was before the flowering period had commenced.

N. H. J. M.

Composition of Buckwheat. By BALLAND (*Compt. rend.*, 1897, 125, 797—799).—The mean yield of buckwheat in the north-west of France is 17 hectolitres per hectare, the mean weight of a hectolitre being 63·09 kilos. Its composition is as follows. Water, 13·00 to 15·20; nitrogenous matter, 9·44 to 11·48; fats, 1·98 to 2·82; sugars and starches, 58·90 to 63·35; cellulose, 8·60 to 10·56; ash, 1·50 to 2·46 per cent.; acidity, 0·044 to 0·096. The mean weight of 1000 grains varies between 17·80 and 21·50 grams. The grains decorticated by hand contain from 19 to 21 per cent. of envelope, and 79 to 81 per cent. of kernel. The composition of this envelope, which is hard and almost unassimilable, is water, 8·50 to 13·30; nitrogenous matter, 3·18 to 3·68; fats, 0·60 to 0·80; extractive matter, 37·05 to 45·22; cellulose, 40·80 to 44·30; ash, 1·40 to 1·80 per cent. The kernel is white, contains very little cellulose, and is readily assimilable; it contains the same nutritive constituents as wheat, and is useful as human food, as well as for cattle.

C. H. B.

Retrograde Phosphoric Acid. By JULIUS STOKLASA (*Ann. Agron.*, 1897, 23, 588—594).—The soluble phosphoric acid of superphosphates can never be present in the form of acid ferrous phosphate, as this decomposes as soon as it is formed, yielding ditriferric phosphates of varying composition, insoluble in water. Ferrous salts, in presence of phosphoric acid soluble in water, always give rise to the production of ditriferric phosphates, unless there is an excess of free phosphoric acid. Acid ferric phosphate can only be present if there is at least 30 per cent. of soluble phosphoric acid in the free state. With less than that amount, acid ferric phosphate may be converted into monoditriferric phosphate.

With soluble phosphoric acid, aluminium salts do not form a compound analogous to those produced by ferrous and ferric salts, but behave like the salts of calcium and magnesium.

A number of pot experiments were made in which barley was grown in (1) a fertile soil containing calcium carbonate (0·63 per cent.) and humus (2 per cent.), and in (2) a soil containing 0·31 and 20·2 per cent. of chalk and humus respectively. Each pot received 0·5 gram of phosphoric acid in the form of a particular salt; different phosphates of calcium, aluminium, and iron were employed.

In soil (1), the acid phosphates of lime, iron, and aluminium give the greatest and similar yields of grain. The trimetallic phosphates had little effect, whilst retrograde phosphoric acid (as normal monometallic phosphate) showed a value equal to half that of the trimetallic phosphate. In soil containing over 5 per cent. of chalk, the results

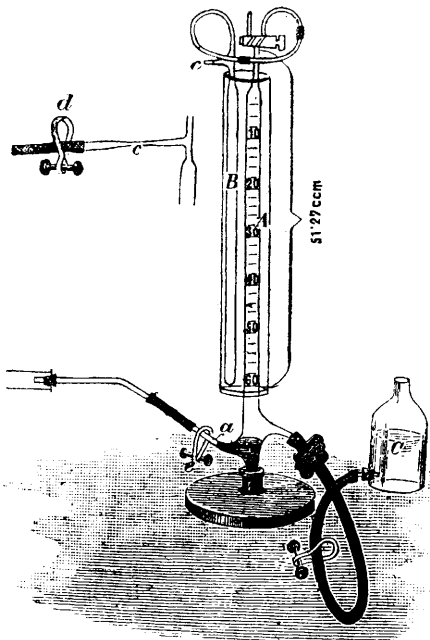
would be different, as the acid phosphates would be transformed into trimetallic phosphates. In presence of much humus (soil 2), retrograde phosphoric acid had a value almost equal to phosphoric acid soluble in water.

N. H. J. M.

Analytical Chemistry.

Gasometric Apparatus. VII. A New Method for the Absolute Measurement of Gases. (Measurement of the Reduced Gas Volume). By OTTO BLEIER (*Ber.*, 1897, 30, 3123—3131. Compare this vol., ii, 136).—Two forms of gas measuring apparatus are

described, which are provided with compensating tubes, by means of which the volume of the gas at 18° and 760 mm. can be directly read off. The first apparatus is specially intended for the estimation of nitrogen, and resembles in general form the usual azotometer, the compensator (B) being connected with the measuring tube (A) at its upper end by a capillary tube, which contains an index of mercury, by means of which it is possible to adjust the gas in the compensating tube to a fixed volume. The measuring tube is graduated so as to give a direct reading in milligrams of nitrogen. The compensator contains a drop of aqueous potash of the strength used in the estimation of nitrogen, and is adjusted in the first instance



by enclosing some definite volume of air in the measuring tube, raising or lowering the reservoir *C* until this occupies the volume which it would have when dry at 18° and 760 mm., and then by means of a side tube *c* making the pressure in the compensator exactly equal to that in the measuring tube. As soon as this is the case, the side tube is sealed and the apparatus is ready for use. The exact position of the mercury index should be determined by actually enclosing various volumes of air in *A*, reducing them to the volume which they would occupy dry at 18° and 760 mm. and observing the average position of the index. The second form of apparatus is intended for use in the same way as Lunge's gas volumeter and can also be employed for general gas analysis. It consists of the two-limbed measuring vessel previously described, combined with a compensator similar in principle to that referred to above. A. H.

Extraction of Liquids. By AUGUSTIN WRÓBLEWSKI (*Zeit. anal. Chem.*, 1897, 36, 671—674).—Two forms of apparatus are described and figured, by means of which a substance can be transferred from an aqueous solution to a lighter, immiscible solvent, such as ether or

light petroleum. The first resembles a Soxhlet's fat extractor, with the addition of a thistle-headed funnel through which the ether flowing from the condenser is conveyed to the bottom of the aqueous layer, and with the syphon tube inserted half-way up the large cylinder, so as to syphon off the ethereal layer only. The second is on a similar principle, but the ether vapour from the distillation flask bubbles up through the aqueous layer also, and the syphon tube is replaced by a simple overflow tube, inserted at a considerable distance above the surface of the aqueous layer.

M. J. S.

Employment of Metallic Sodium, Magnesium, and Aluminium in Qualitative Analysis. By WALTHER HEMPEL (*Zeit. anorg. Chem.*, 1898, 16, 22—25).—Metallic sodium is conveniently employed in blowpipe-analysis for the reduction of tin oxide to metallic tin, barium sulphate to barium sulphide, and similar operations. A small piece of freshly-cut sodium is pressed out into a thin sheet on a piece of filter paper, and the substance to be analysed is rolled up in this so that two layers of filter paper are on the outside. The small cylinder is then wound round with thin iron wire and heated in a reducing bunsen-burner flame; the action is complete in a few minutes, and the spiral of wire is then pushed into the tube of the burner and allowed to cool in the gas. The cold product is separated from the iron wire and ground in an agate mortar with water, when the reduced metal is easily separated and identified by the usual methods. When the samples for analysis contain silicic or boric acid, the product of the action contains silicon or boron; in this case, it is treated with hydrochloric acid, when the sulphides, if they are present, are detected by lead paper, and the insoluble residue is then washed with water, dried, and heated on a piece of platinum foil, when a mixture of silica and boron trioxide mixed with black silicon or boron is obtained.

When it is necessary to examine the spectrum given by the product of the reaction, metallic magnesium or aluminium should be employed in place of sodium, the sample being mixed with the powdered metal, and rolled in a piece of filter paper and ignited as described above. The product, when dissolved in hydrochloric acid, gives very good flame reactions.

E. C. R.

Application of Acid Solutions of Arsenious Acid in Volumetric Analysis. By M. BIALOBRZESKI (*Chem. Centr.*, 1897, 1, 259—260; from *Pharm. Zeit. Russ.*, 35, 785—789).—The author has found that the reaction between iodine and arsenious acid takes place quantitatively in the presence of an acetate and free acetic acid at a temperature of about 70°. To estimate the available chlorine in bleaching powder, the prepared solution is mixed with an excess of standard arsenious acid dissolved in ammonium acetate; after acidifying with acetic acid and warming to 60°, the excess of arsenic is titrated with standard iodine. Chlorates may be estimated by first adding excess of the arsenic and then excess of hydrochloric acid; the liquid is afterwards neutralised with ammonia, acidified with acetic acid, and titrated with iodine. Peroxides may be estimated in a similar manner by gently heating them with hydrochloric acid in the presence of an excess of the arsenical solution and titrating the latter as directed. The process may also be applied to chromates and to the indirect estimation of lead.

L. DE K.

Employment of Normal Sodium Oxalate in Volumetric Analysis. By S. P. L. SÖRENSEN (*Zeit. anal. Chem.*, 1897, **36**, 639—643).—For the preparation of standard acids with the greatest accuracy, it is an objection to the use of sodium carbonate that it cannot be preserved anhydrous, and that it loses carbonic anhydride on ignition. Sodium oxalate is easily prepared pure; the commercial salt is dissolved in 32 parts of water, the solution made feebly alkaline with soda and allowed to clarify completely; the solution is then evaporated on the water bath to 1/10, the sodium oxalate separating and potassium oxalate remaining in solution. The salt is washed on a suction filter, and recrystallised until the mother liquor is free from chlorides, sulphates, and alkali; the final crystallisation is best performed by running the hot solution into alcohol, as the salt thus obtained does not decrepitate on ignition. Dried at 125—150°, it is anhydrous and not hygroscopic. For use, a weighed quantity is ignited in a platinum crucible, either burning off the separated carbon by fusing the alkaline residue with access of air, or filtering it off after the addition of a very small excess of the acid under examination. Both methods give exactly the same result, no loss of sodium being observable during the fusion.

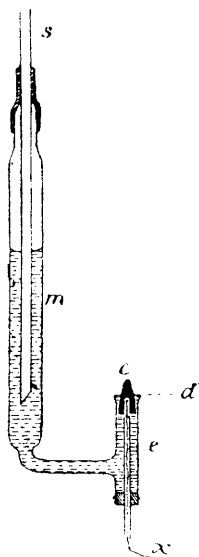
In six experiments (using three different preparations of oxalate) the greatest deviation from the mean was less than 1/1100 of the total amount.

For standardising permanganate, this salt is to be preferred to either oxalic acid or ammonium oxalate.

M. J. S.

Apparatus for the Spark Spectrum of Solutions. By LOUIS M. DENNIS (*Zeit. anorg. Chem.*, 1898, **16**, 19—21).

—The advantages of the apparatus are that the splashing on to the slit of the spectroscope is easily obviated, and there is very little waste of the solution which is being examined. The apparatus consists of a short, vertical tube connected with a longer tube bent at right angles, the long arm being about four times the length of the shorter. The shorter arm is open at both ends, and the lower end carries a cork, through which passes a glass tube enclosing a platinum wire which is connected at the top of the arm with a graphite pole arranged at such a height that when the short arm is maintained full of the solution there is a constant supply of the solution to the pole. The longer arm of the apparatus, which acts as a reservoir for the solution, is closed at the top by a piece of rubber tube, through which a glass tube, open at both ends, slides, and can be adjusted so that the height of the bottom of the tube is level with the top of the shorter arm; by this arrangement, as in a Mariotte's bottle, the solution in the shorter arm is kept at a constant level. The slit of the spectroscope is protected from splashes by placing before it a sheet of glass.



E. C. R.

Kjeldahl's Process. By JAMES O'SULLIVAN (*J. Soc. Chem. Ind.*, 1897, 16, 111—112).—Employing an acid consisting of one part of strong sulphuric acid and two parts of Nordhausen acid, adding 0.5 gram of mercuric oxide at the commencement, and completing the oxidation with potassium permanganate, the author has obtained, in the analysis of malt extract and ale, results agreeing accurately with those of the Dumas' nitrogen method. M. J. S.

Volumetric Estimation of the Nitro-group in Organic Compounds. By STEWART W. YOUNG and R. E. SWAIN (*J. Amer. Chem. Soc.*, 1897, 19, 812—814).—When nitro-derivatives are heated with a hydrochloric acid solution of stannous chloride, the following reaction takes place: $R \cdot NO_2 + 3SnCl_2 + 7HCl = NH_2R, HCl + 3SnCl_4 + 2H_2O$. The authors have so far proved this to be the case with dinitrobenzene. On account of the instability of stannous chloride, the operation is performed in a current of carbonic anhydride, the nitro-compound being first dissolved in alcohol. After two hours' action, the excess of stannous chloride is titrated with standard iodine. (See this vol., ii, 192.) L. DE K.

Gasometric Estimation of Nitrous Acid. By E. RIEGLER (*Zeit. anal. Chem.*, 1897, 36, 665—668).—The method depends on the oxidation of the nitrous acid to nitric acid by acidified hydrogen peroxide, and the estimation of the excess of the peroxide by treatment with permanganate and measuring the oxygen evolved.

The author employs the Knop-Wagner azotometer. Five c.c. of a 1 per cent. hydrogen peroxide solution, mixed with 30 c.c. of water and 10 c.c. of strong sulphuric acid, is decomposed by about 0.1 gram of potassium permanganate with the usual precautions, and the volume of oxygen read off. Immediately afterwards, the nitrite solution, containing not more than 0.05 gram of N_2O_3 in 30 c.c. of solution, is mixed in the decomposing flask with 5 c.c. of the same hydrogen peroxide and a few drops of sulphuric acid. After shaking and waiting five minutes, 10 c.c. of strong acid is cautiously added, and the decomposition with permanganate carried out as before. The difference between the two volumes of oxygen expressed in cubic centimetres at 0° and 760 mm. is multiplied by 0.0017 to obtain grams of N_2O_3 . Instead of permanganate, silver oxide may be used, the hydrogen peroxide being mixed with potassium hydroxide, and silver nitrate being placed in the inner vessel. In this case, twice as much peroxide is employed, and the multiplier is 0.0034.

M. J. S.

Estimation of Phosphorus in Steel. By R. W. MAHON (*J. Amer. Chem. Soc.*, 1897, 19, 792—795).—The process described is a modification of the method recently introduced, by which the yellow phosphomolybdate precipitate is titrated with standard alkali and acid, using phenolphthalein as indicator. The author has, as yet, only used it for samples low in silicon and carbon, when, under favourable conditions, an assay may be made in eight minutes.

Whilst the drillings are being got ready, 70 c.c. of water and 30 c.c. of nitric acid of sp. gr. = 1.4 is put into an Erlenmeyer flask, the

burettes are filled with the respective alkali and acid, and a filter is connected with the filter-pump. Four grams of the drillings is then put into the acid and heated over a gas-burner. When dissolved, 3 c.c. of a standard potassium permanganate is added, and the liquid is boiled until no longer pink; 10 c.c. of hydrochloric acid of sp. gr. = 1.20 is then added, and the boiling continued until the liquid is clear. After cooling for a few seconds, 50 c.c. of molybdate solution and 15 c.c. of ammonia of sp. gr. = 0.90 are added, care being taken not to let them run along the sides of the flask. After shaking for 15 seconds, the precipitate is collected on the filter, washed with cold water, and then placed in a small beaker containing a known volume of the alkali, the excess of which is then titrated with standard acid.

The molybdate solution is made by dissolving 100 grams of molybdic acid in a mixture of 200 c.c. of water and 200 c.c. of ammonia of sp. gr. = 0.90; the solution is then filtered into 1250 c.c. of nitric acid of sp. gr. = 1.20, blowing air through the mixture. L. DE K.

Estimation of Insoluble Phosphorus in Iron Ores. By CHARLES T. MIXER and HOWARD W. DUBOIS (*J. Amer. Chem. Soc.*, 1897, 19, 614—619).—By insoluble phosphorus is understood that phosphorus which cannot be extracted by boiling hydrochloric acid of sp. gr. = 1.1 from the silicious residue left after the acid treatment of iron ores. The authors, however, find that this modification of phosphorus becomes readily soluble if the residue is ignited.

The details are as follows. 1.5 grams of the ore is dissolved in 25 c.c. of hydrochloric acid, and the excess of acid is removed by evaporating until the mass becomes syrupy. Water is then added, and the insoluble matter collected, washed, and ignited. Five minutes boiling of the ignited residue with dilute hydrochloric acid will now dissolve the remainder of the phosphorus, which is probably present as an aluminium compound. L. DE K.

Qualitative Analysis of Phosphates. By ROBERT M. CAVEN (*J. Soc. Chem. Ind.*, 1897, 16, 208—209).—When, in the course of a qualitative analysis, the precipitate produced by ammonia contains phosphates, it is redissolved in the least possible quantity of hydrochloric acid, and much ammonium acetate is added with a little acetic acid; any precipitate produced (FePO_4 , AlPO_4 , CrPO_4) is collected. To the filtrate, ammonium phosphate is added as long as it produces a precipitate, this being collected on the same filter as before; this precipitate is examined for iron, chromium, and aluminium by fusion with pure potassium hydroxide. The filtrate is freed from the excess of phosphate by adding ferric chloride until the precipitate produced remains brown, and then boiling for several minutes; the solution will then be free from iron also, and the alkaline earths, &c., will be detected by the usual methods. Since chromium phosphate is not completely insoluble in acetic acid, a little chromium may be found in the precipitate produced by ferric chloride. M. J. S.

Estimation of Phosphoric Acid by Titration of the Ammonium Phosphomolybdate Precipitate with Standard Alkali. By B. W. KILGORE (*J. Amer. Chem. Soc.*, 1897, 19, 703—711. Compare Abstr., 1896, 335).—The author having used this process for a

considerable time, recommends it as being thoroughly trustworthy. It must, however, be remembered that the yellow phosphomolybdate precipitate is an acid salt, and not altogether insoluble in water; any attempt, therefore, to absolutely free it from acidity must fail, as this will cause, not only a chemical, but also a mechanical loss. The washing should, therefore, be done with small quantities of water, using altogether 150, or at most not more than 200 c.c.

L. DE K.

Analysis of Silicates. By A. LECLERE (*Compt. rend.*, 1897, 125, 893—894).—Silicates are decomposed when fused with about three times their weight of lead oxide, and when the cooled product is treated with not less than ten times its weight of a mixture of equal volumes of ordinary nitric acid and fuming nitric acid at about 40°, the silica separates completely in a partially hydrated but non-gelatinous form, together with lead nitrate. On diluting with water, the lead nitrate dissolves, and the silica is readily filtered and washed. The filtrate is concentrated and mixed with alcohol and a slight excess of hydrochloric acid, which completely precipitates the lead as chloride. The fusion with lead oxide can be carried out without risk in a platinum crucible, if the latter is heated in a muffle so that reducing gases are excluded, and the oxide is prepared in the following way. An excess of a saturated solution of oxalic acid containing about 3 per cent. of nitric acid is added to a 15 per cent. solution of lead nitrate, and the precipitate of oxalonitrate is dried and heated to dull redness in a porcelain dish; about a quarter of it is then moistened with nitric acid, well mixed with the remainder, and the heating continued.

C. H. B.

Estimation of Carbon in Iron. By E. HARBECK and GEORG LUNGE (*Zeit. anorg. Chem.*, 1898, 16, 67—75).—The authors review the principal methods for the estimation of carbon in iron, and compare the results they have obtained in this investigation. They conclude that Wöhler's chlorine method and Corleis' method give accurate results, which closely agree with each other; the method described by Lunge and Marchlewski gives results somewhat lower than those obtained by Corleis' method; the results are better in the analysis of steel when copper ammonium chloride is substituted for copper sulphate, although the error is not entirely eliminated. In the case of cast iron, however, the improvement obtained by using copper ammonium chloride is so small as to be valueless. The ordinary copper ammonium chloride method gives results which are no better than those obtained by Lunge and Marchlewski's method, and takes considerably more time. Although Corleis' method is the best when very accurate results are required, for ordinary commercial purposes Lunge and Marchlewski's method is quickest and most convenient, but it must be remembered that there is a constant loss of about 0.03 per cent. of the carbon.

E. C. R.

Flue Gases in Relation to Furnace Efficiency. By P. FRITZSCHE (*Zeit. anal. Chem.*, 1897, 36, 669—671).—In estimating the efficiency of the fuel burnt in a furnace, it is necessary to know the composition of the fuel as well as that of the flue gases, and in

many cases it would be convenient to deduce the former from the latter. Lunge's formula (*Zeit. angew. Chem.*, 1889, 240) for this relates only to fuels containing no hydrogen (coke, anthracite). If, however, the water in the flue gas is estimated, as well as the carbonic anhydride, carbonic oxide, and oxygen, a formula can be developed which applies to all ordinary fuels. This is conveniently done by aspirating 5—10 litres of the flue gas through a weighed calcium chloride tube.

Expressing by n the nitrogen, h the carbonic anhydride, k' the carbonic oxide, and o the free oxygen, all in volumes per cent.; by f the total water, f'' the water derived from h the available hydrogen of the fuel, f''' the hygrometric water of the atmospheric air, ϕ the water pre-existing in the fuel, all expressed in grams per cubic metre of dry flue gas :— $f - (f'' + f''') = \phi$ and

$$f' = \left[\left\{ \frac{n}{3.76} - \left(h + \frac{k'}{2} + o \right) \right\} 1.429 \times \frac{9}{8} \right] : 100.$$

Also $h = \frac{f'}{9}$. The ratio of the carbon to the available hydrogen and the pre-existing water of the fuel must be the same in the fuel as in the flue gases. In the gases, the ratio is $\frac{0.539 (k + k')}{100} : h : \phi$. Putting

a for the ratio of carbon to hydrogen, and b for that of carbon to water, and denoting by K the carbon in 1 kilogram of fuel free from ash,

$$K = \frac{1}{1 + \frac{1}{a} + \frac{1}{b}}. \quad \text{From the value of } K \text{ thus ascertained, the}$$

amount of flue gas derived from 1 kilogram of fuel is calculated in the usual manner. If regard is to be paid to the sulphur in the fuel, the sulphurous anhydride in a cubic metre of flue gas is denoted by s , and putting c for the ratio of carbon to sulphur,

$$f' = \left[\left\{ \frac{n}{3.76} - \left(h + \frac{k'}{2} + o + s \right) \right\} 1.429 \times \frac{9}{8} \right] : 100, \text{ and}$$

$$K = \frac{1}{1 + \frac{1}{a} + \frac{1}{b} + \frac{1}{c}}.$$

M. J. S.

Behaviour of Platinochlorides. By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1897, 15, 412—418).—The estimation of potassium in minerals which, like kainite, contain potassium, sodium, magnesium, calcium, and barium as sulphates and chlorides, is effected by taking advantage of the greater solubility of the chlorides in methylic than in ethylic alcohol. Barium chloride is soluble in 78 parts of methylic alcohol (sp. gr. = 0.790) and in 7000 parts of ethylic alcohol (sp. gr. = 0.8035). The solution of the mineral is treated with a slight excess of barium chloride to precipitate all the sulphuric acid, the clear solution evaporated to a syrup with platinic chloride, and then extracted with methylic alcohol. The sodium, magnesium, and calcium platinochlorides are easily dissolved, and the barium salt is decomposed into platinic chloride and barium chloride, and these salts are also dissolved by the methylic alcohol, leaving a residue of pure potassium

platinochloride, which is finally washed with ether. The results of the analysis agree closely with those obtained by reduction of the potassium platinochloride by R. Fresenius' method. E. C. R.

Modified Method of Fine Silver Assay. By AUGUSTUS E. KNORR (*J. Amer. Chem. Soc.*, 1897, 19, 814—816).—About 1 gram of standard silver is dissolved in a little dilute nitric acid (1 : 2) and heated until all the nitrous acid has been expelled. A standard solution of salt is then added until the bulk of the silver is precipitated, and after thoroughly shaking, the silver chloride is removed by filtration, and the last traces of the silver are then precipitated by means of a standard solution of potassium thiocyanate, using ferric ammonium sulphate as indicator.

The solutions having been thus standardised, are ready for the assay of any given sample of silver. The impurities commonly present in fine silver do not interfere with the process. L. DE K.

Volumetric Estimation of Lime in Sugar Liquors. By N. FRADISS (*Chem. Centr.*, 1897, i, 262—263; from *Bull. Assoc. Chimistes*, 14, 22).—100 c.c. of the juice, or syrup, is mixed with excess of ammonia and ammonium oxalate, and boiled for 2 hours. The precipitate, after being collected on a filter and well washed, is dissolved in dilute sulphuric acid and titrated, in the usual way with potassium permanganate. L. DE K.

Quantitative Separation of Barium, Strontium, and Calcium. By SIDNEY G. RAWSON (*J. Soc. Chem. Ind.*, 1897, 16, 113—115).—Calcium nitrate is soluble in concentrated nitric acid, the nitrates of the other two metals being absolutely insoluble. The solution of the mixed nitrates is therefore evaporated to dryness, and the residue digested with nitric acid of 70—80 per cent. The barium and strontium are subsequently separated by the chromate method in acetic acid solution (*Abstr.*, 1893, ii, 436). M. J. S.

Rapid Valuation of Zinc Dust. By ANDRÉ R. WAHL (*J. Soc. Chem. Ind.*, 1897, 16, 15).—Half a gram of the zinc dust is shaken with 25 c.c. of cold water, and 7 grams of pure neutral ferric sulphate is added. In a quarter of an hour the zinc will have dissolved (with the exception of impurities), with reduction of an equivalent quantity of the ferric salt, and without evolution of hydrogen if acid is absent. The solution is then acidified, and titrated with permanganate. The ferric sulphate is prepared by oxidising a mixture of 5 parts of ferrous sulphate and 1 of sulphuric acid by excess of nitric acid, evaporating to dryness, grinding, and washing with alcohol until no longer acid, and drying thoroughly. A blank assay is desirable. M. J. S.

Electrolytic Detection of Lead in Urine. By P. WEINHART (*Chem. Centr.*, 1897, i, 129; from *Pharm. Centr. Halle*, 37, 759—760).—The urine is evaporated on the water bath to half its bulk, mixed with 65 per cent. of nitric acid, and then evaporated to dryness; the residue, taken up with a little nitric acid, is diluted to a litre, heated to 50°, and submitted to electrolysis. The presence of lead is indicated by the deposition of a film of brown lead dioxide on the positive electrode. L. DE K.

Acetylene as a Quantitative Reagent. By HENRIK G. SÖDERBAUM (*Ber.*, 1897, 30, 3014—3017. Compare *Abstr.*, 1897, ii, 348).—*Separation of Copper from Cadmium.*—The solution, about 150 c.c. in volume, is mixed with 10—15 c.c. of strong aqueous sulphurous acid, and then with 20—25 c.c. of ammonia (sp. gr. = 0.96), warmed on the water bath until it is only faintly blue, and then treated with a current of acetylene gas. The precipitate of copper acetylide is washed 2—3 times by decantation with dilute ammonia saturated with acetylene, and then on the filter with hot water; it is decomposed with nitric acid, and the copper nitrate formed is ignited, and the residue of oxide weighed. The cadmium in the filtrate is determined electrolytically, or by precipitation and weighing as the sulphide.

Separation of Copper from Arsenic.—The solution is treated as in the preceding case, except that enough sodium hydroxide must be added to combine with the arsenious or arsenic acid; when ammonium salts alone are present, traces of arsenic are precipitated along with the copper. The arsenic in the filtrate is determined by oxidising it (if necessary) to arsenic acid, with nitric acid, precipitating it as magnesium ammonium arsenate, and either weighing this, or igniting it and weighing as magnesium pyroarsenate.

The usual error in the determinations quoted was a deficit of about 0.3 per cent. of the total quantity in the case of each metal. An acid solution of mercuric chloride is very efficient in freeing acetylene from hydrogen phosphide (it was recommended for this purpose by Bergé and Reychler), but in the determinations described, there is no actual need to free the acetylene from this impurity. C. F. B.

Modification of the Permanganate Method for the Estimation of Iron. By HAMILTON P. CADY and ALFRED P. RUEDIGER (*J. Amer. Chem. Soc.*, 1897, 19, 575—581).—The following reagents are required. *A.* A 5 per cent. solution of stannous chloride, which should give no deposit when it is diluted with twenty times its bulk of water and boiled; a little free hydrochloric acid and a few fragments of tin will keep it in good condition. *B.* Hydrochloric acid, made by mixing equal volumes of water and acid of sp. gr. = 1.2. *C.* A solution of mercuric sulphate, made by mixing 200 grams of the salt with 80 c.c. of sulphuric acid, and adding this to 800 c.c. of water; after adding a solution of 100 grams of orthophosphoric acid, the liquid is made up to 1 litre.

1st Method.—The iron ore, after being completely decomposed by boiling with 10—15 c.c. of the acid *B*, is diluted to 100 c.c. and reduced by adding to the boiling liquid solution *A* until no thiocyanate reaction is obtained; the slight excess of tin is carefully oxidised by potassium permanganate, and then a few drops only of the tin are added. After cooling, 50 c.c. of dilute sulphuric acid is added, and then, for every 10 c.c. of *B*, 35 c.c. of *C* is added; the whole is made up to 400 c.c., and titrated with permanganate. *2nd Method.*—To the acid solution, 2 c.c. of *C* is added, the liquid is heated to boiling and *A* is added until a permanent turbidity is produced. The whole is then diluted to 300 c.c., 50 c.c. of dilute sulphuric acid, and 45 c.c. of *C* are added, and the iron is at once titrated with permanganate.

L. DE K.

Electro-analysis of the Metals of the Ammonium Sulphide Group. By M. ENGELS (*Chem. Centr.*, 1897, i, 258—259; from *Chem. Rundschau.*, 1896, 20—24).—Iron may be separated from manganese by dissolving the mixed sulphates in water contained in a platinum dish which serves as cathode; the anode being a platinum spiral which is immersed in a beaker filled with water, the two vessels communicating by means of an inverted U-tube filled with the liquid. After acidifying with sulphuric acid, the liquid is electrolysed with a current of 0.4—0.8 ampère and 40—60 volts., while hydrogen is passed through the beaker to prevent the formation of permanganic acid; after 12 hours, all the manganese is precipitated, as peroxide, on the anode.

Iron may be separated from aluminium by electrolysing in the presence of an alkaline solution of potassium sodium tartrate, avoiding a large excess of the latter. From nickel, it is best separated in an ammoniacal solution, using a current not exceeding 1 ampère. The nickel is completely precipitated, and is free from iron, if only care has been taken to thoroughly oxidise the latter by means of hydrogen peroxide. In the same manner, nickel may be separated from manganese. The author did not succeed in separating iron from chromium or cobalt.

L. DE K.

Iodometric Estimation of Molybdenum. By HANS EULER (*Zeit. anorg. Chem.*, 1897, 15, 454—455).—A reply to the criticisms of F. A. Gooch (this vol., ii, 54).

Titration of Stannous Salts with Iodine. By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1897, 19, 809—812).—The author has found that stannous chloride may be accurately titrated in a dilute hydrochloric acid solution by means of standard iodine, using starch as indicator. The potassium iodide, used to dissolve the iodine, should be free from iodate, and the iodine solution should be standardised against a solution of tin of known strength, which has been itself checked by means of a standard solution of potassium dichromate. The tin solution may be kept unaltered for some time by covering it with a layer of paraffin oil.

L. DE K.

Qualitative Separation of Arsenic, Antimony, and Tin. By SIDNEY G. RAWSON (*J. Soc. Chem. Ind.*, 1897, 16, 113).—The author advocates Clarke's oxalic acid method, carried out as follows. The washed sulphides are boiled with a small quantity of hydrochloric acid to which a drop of nitric acid is added; this will often suffice to prove the presence of arsenious sulphide, which dissolves with greater difficulty than those of antimony and tin. A strong solution and crystals of oxalic acid are then added, so as to obtain a saturated solution when hot, and hydrogen sulphide is passed through it, when antimony and arsenic are precipitated, whilst the tin remains dissolved. To the filtrate, ammonia is added, and if a precipitate is produced this is redissolved by cautious addition of ammonium sulphide; on adding acetic acid, the tin is precipitated as a mixture of oxide and sulphide. The antimony and arsenic are best distinguished by Hofmann's well known method of passing their hydrides through silver nitrate.

M. J. S.

Separation of Thorium from Cerium. By ERNST HINTZ and HERMANN WEBER (*Zeit. anal. Chem.*, 1897, 36, 676—685).—Fresh experiments on the separation of thorium from cerium by boiling with sodium thiosulphate (see Abstr., 1896, ii, 677) have shown that with dilute solutions the separation is very nearly perfect, only traces of each metal remaining with the bulk of the other. With strong solutions, the errors are somewhat greater, but still negligible. A re-examination of the ammonium oxalate method (Abstr., 1897, ii, 162) shows that it is far less efficient for separating these metals, and Glaser's modification (Abstr., 1897, ii, 349) is no improvement.

M. J. S.

Value of a Bacteriological Examination of Water from a Sanitary Point of View. By E. K. DUNHAM (*J. Amer. Chem. Soc.*, 1897, 19, 591—605).—The paper deals chiefly with the detection of the colon bacilli. As these cannot multiply when putrefying organic matters are absent, a considerable quantity of them may be safely said to indicate an objectionable pollution of the water, although a chemical examination may not point to the presence of excreta.

L. DE K.

Quantitative Separation of Ethylene and Benzene Vapour. By E. HARBECK and GEORG LUNGE (*Zeit. anorg. Chem.*, 1898, 16, 26—49).—The method is based on the conversion of ethylene into ethane by means of hydrogen in the presence of platinum black. The apparatus employed, which is fully described in the original paper, consists essentially of a capillary tube charged with platinum black so arranged that the sample of gas can be passed through it forwards and backwards two or three times; the platinum black must be saturated with hydrogen at the temperature at which the reaction with ethylene is to take place, the most advantageous temperature being 90—100°. The estimation of the ethylene and benzene in a sample of gas is performed as follows. In a sample of the gas, the ethylene and benzene are estimated together by absorption with fuming sulphuric acid, and the other constituents in the sample are then estimated by the ordinary methods. In a second sample of the gas, the oxygen and acetylene are removed, and the remainder of the sample, which must contain excess of hydrogen, is passed two or three times through the capillary tube charged with platinum black and then treated with fuming sulphuric acid. The quantity absorbed by the sulphuric acid gives the benzene, and the difference between this and that absorbed by direct treatment with sulphuric acid gives the ethylene. Or the ethylene can be estimated in the sample after removal of the oxygen and acetylene by measuring the contraction which takes place on treating the gas with platinum black and hydrogen. This method has, unfortunately, only a very limited application, because the presence of a small quantity of carbonic oxide prevents the reaction between the ethylene and the hydrogen.

The estimation of benzene in coal gas and similar mixtures is effected by passing about 10 litres of the gas through a mixture (110 c.c.) of equal weights of concentrated sulphuric and fuming nitric acids contained in an inclined tube consisting of ten glass

bulbs. After the passage of the gas, the acid mixture is poured into water and ice, well cooled with ice, and neutralised with sodium hydroxide. By this means, the dinitrobenzene is obtained as a white, crystalline precipitate which is separated by filtration and washed with water. The filtrate and wash water are made up to a convenient bulk and an aliquot part extracted with ether, the extract separated, evaporated to dryness, and the residue extracted with absolute ether; this ethereal solution, which contains any dinitrobenzene which may have remained in the aqueous filtrate, is evaporated to dryness and the residue weighed. The dinitrobenzene is dried at 70–80° and weighed, the weight being corrected for the quantity extracted from the filtrate by ether. The ethylene present in the gas is also absorbed in the mixed acids, but the products are soluble in water and are not extracted from the aqueous solution by ether.

E. C. R.

Estimation of Glycerol. By BOULEZ (*Zeit. anal. Chem.*, 1897, 36, 719–720; from *Bull. soc. chim. Nord France*, 4, 115).—The glycerol is converted into glycerophosphoric acid by trituration with twice its weight of phosphoric anhydride and heating for 7 hours at 130–135°; when cool, the syrupy mixture is dissolved in 20 parts of water and triturated with 10 parts of precipitated calcium carbonate. After 12 hours, with frequent stirring, the calcium glycerophosphate is filtered from the calcium phosphate and excess of carbonate, which are washed with cold water, and the phosphoric acid in the filtrate is estimated by ordinary methods. For impure glycerol, some calcium chloride is added after the calcium carbonate.

M. J. S.

Fehling's Solution. By MAX SIEGFRIED (*Ber.*, 1897, 30, 3133–3134).—The author points out, in reply to Jovitschitsch (this vol., ii, 98) and Gerock (this vol., ii, 147), that the reduction experienced when Fehling's solution, to which some acid has been added, is boiled, is due entirely to the absence of alkali and not to the specific action of the acid or the salt formed by it with the alkali present.

A. H.

Detection of Cane-sugar. By GIORGIO PAPASOGLI (*Zeit. anal. Chem.*, 1897, 36, 715; from *Bull. assoc. chim. sucrerie et distillerie*, 13, 68).—The aqueous solution is treated with a few drops of a solution of a cobalt salt and a small excess of sodium hydroxide, whereupon an amethyst-violet colour is produced. Grape-sugar yields a blue, passing into dirty green. One part of cane-sugar mixed with 9 parts of grape-sugar can be detected. Coloured liquids must be decolorised, and gum and dextrin, which would obscure the sugar reaction by giving a permanent blue, must be precipitated by ammoniacal lead acetate or baryta.

M. J. S.

Estimation of Sugar in Sweet Wines. By J. PINETTE (*Chem. Zeit.*, 1897, 21, 395).—The sample is treated, as usual, with Fehling's solution, but instead of reducing the cuprous oxide in a current of hydrogen and weighing the metallic copper, the amount of copper is determined by titration.

The filter containing the cuprous oxide is put back into the beaker, opened by means of a rod, moistened with 5 c.c. of strong nitric acid,

and 10 c.c. of strong ammonia is added. After the paper has been well broken up, a standardised solution of potassium cyanide is run in until the liquid is colourless. Towards the end, a few drops of potassium ferrocyanide solution (1:20) are introduced, and the cyanide solution is added very slowly. The cyanide solution should contain about 60 grams of the salt per litre, and must be standardised by means of metallic copper; this should not vary much in weight from that of the cuprous oxide, and the same quantity of nitric acid and ammonia must be used.

L. DE K.

Estimation of Sugar in Chocolate. By XAVIER ROCQUES (*Chem. Centr.*, 1897, i, 268; from *Revue intern. falsific.*, 9, 198).—Fifteen grams of the sample is heated with 90 c.c. of water to 40° and well shaken, 15 c.c. of a 10 per cent. solution of lead acetate is added, and the liquid filtered into a graduated measure; 70 c.c. of the filtrate is then mixed with 10 c.c. of acetic acid and 20 c.c. of a 10 per cent. solution of sodium sulphate to remove the excess of lead. The filtrate now contains all the cane-sugar and also any glucose, which can be estimated in the usual way. To invert the cane-sugar, it is sufficient to dilute 50 c.c. of the filtrate with 450 c.c. of water and heat the mixture in the water bath for 3 hours. Dilute acetic acid has no hydrolysing action on dextrin.

L. DE K.

Estimation of Starch in Cereals. By JEAN EFFRONT (*Chem. Centr.*, 1897, i, 202—203; from *La Bière*, 4, 145).—Three grams of the finely ground sample is extracted with ether and well rubbed up in a mortar with 20 c.c. of strong hydrochloric acid, which should be gradually added. When the starch is dissolved, water is added to make it up to 100 c.c. After filtering, 75 c.c. of the liquid is exactly neutralised with aqueous soda, avoiding even the faintest alkalinity, then 0.2 c.c. of normal acid is added, the liquid evaporated to one-half on the water bath, and introduced into a 75 c.c. flask. After making up to the mark and filtering a few times through asbestos, the liquid is polarised in a 40 cm. tube, whilst another portion is titrated with Fehling's solution. From the rotation, the amount of dextrin (or starch) may be easily calculated, but allowance must be made for the glucose, which has only 1/3.7 of the rotatory power of dextrin.

L. DE K.

Estimation of Farinaceous Matter in Sausages. By JOSEPH MAYRHOFER (*Chem. Centr.*, 1897, i, 204—205; from *Forsch. Ber. Lebensm.*, &c., 3, 429—430. Compare *Abstr.*, 1897, ii, 525).—From 10 to 20 grams of the sample is heated at 100° with 50 c.c. of an 8 per cent. alcoholic solution of potash until the meat has dissolved; the mixture is then diluted with proof spirit, and the insoluble portion collected on a filter and washed first with hot alcoholic potash and then with alcohol, until the filtrate no longer gives any turbidity on acidifying. The filter with the insoluble matter is now put back into the beaker, and, after being treated for half an hour on the water bath with 60 c.c. of normal potash and allowed to cool, is acidified with acetic acid, and water added to make the whole up to 100 c.c. In an aliquot part of the liquid, the starch is then precipitated by adding an equal volume

of strong alcohol; the precipitate is collected, and after being washed first with proof spirit, then with strong alcohol, and finally with ether, is dried and weighed.

L. DE K.

Detection of Formalin in Milk. By K. FARNSTEINER (*Chem. Centr.*, 1897, i, 133—134; from *Forsch. Ber. Lebensm.*, &c., 1896, 3, 363—370).—The author thinks that the various tests for the detection of formaldehyde in milk should be applied, not only to the milk itself, but also to its distillate. The best test is no doubt sulphuric acid containing a trace of iron; when applying this to the distillate, some casein should be added (Hehner).

L. DE K.

Detection and Estimation of Acetone in Urine. By LOUIS WILLEN (*Chem. Centr.*, 1897, i, 134; from *Schweitz. Woch. Pharm.*, 34, 433—436).—From 300—500 c.c. of the sample is mixed with 30—50 c.c. of dilute sulphuric acid, and submitted to distillation until 60 c.c. has distilled over; by carefully determining the specific gravity, the quantity of acetone may be calculated from the tables given in the paper. The presence of acetone is then confirmed by the well-known iodoform reaction.

L. DE K.

Simplification of Hopkins' Method for Estimating Uric Acid in Urine. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1897, 24, 224—245).—Ten grams of ammonium sulphate is added to 100 c.c. of urine, and after the mixture has been allowed to remain for 2 hours, the precipitated ammonium urate is washed with a 10 per cent. solution of ammonium sulphate until the washings are free from chlorine. The urate is then dissolved in sulphuric acid and titrated with potassium permanganate in the usual way; an addition of 1 milligram per 100 c.c. of filtrate being made to the end result as a correction for the solubility of the ammonium urate.

W. D. H.

Rapid Estimation of Uric Acid in Urine. By E. H. BARTLEY (*J. Amer. Chem. Soc.*, 1897, 19, 649—656).—The author, after pointing out the defects in the various processes for estimating uric acid in urine, now recommends the following: 100 c.c. of the sample, mixed with 5 c.c. of magnesia mixture and 10 c.c. of ammonia of sp. gr. = 0.960, is heated on the water bath, and N/50 normal silver nitrate is then run in from a burette, a few drops of the liquid being, from time to time, filtered through a miniature cotton filter, and tested for excess of silver by means of a solution of sodium hydrogen sulphide. From the result, 1 c.c. is deducted, that being the amount of silver which will be in excess before any reaction is observed. Each c.c. of silver solution is equivalent to 0.00336 gram of uric acid.

L. DE K.

A New Volumetric Method of Estimating Uric Acid in Urine. By FRANCIS WHITTAKER TUNNICLIFFE and OTTO ROSENHEIM (*Brit. Med. J.*, 1898, i, 364).—Uric acid obtained from the urine by Hopkins' method, is suspended in water which is kept boiling, a few drops of alcoholic phenolphthalein are then added, and a N/20 solution of piperidine is run in; the complete saturation of the uric acid present is indicated by the presence of a red coloration, which remains on shaking, and also by the fact that no uric acid remains undissolved.

W. D. H.

Mechanical Arrangement of Fat Extraction Apparatus. By GUSTAVE J. VOLCKENING (*J. Amer. Chem. Soc.*, 1897, 19, 735—738). This is an ingenious arrangement for using Soxhlet's tubes in which fatty materials are being extracted with ether. The flasks containing the latter are heated on gun-metal steam tables on which small capsules partly filled with water have been placed; or a damp piece of thin felt may be used. The arrangement, which is fully illustrated, will be found very useful to analysts who have to make many fat estimations with but limited space in their laboratories. L. DE K.

A Simple Fat Extractor. By VERNON J. HALL (*J. Amer. Chem. Soc.*, 1897, 19, 586).—The apparatus consists of a small shallow dish made of very light copper and furnished at the bottom with two tightly fitting caps, one of which is shallow whilst the other resembles a Gooch's crucible. When required for use, the shallow cap is fitted on, 5 c.c. of milk is introduced into the previously weighed apparatus, and after drying for half-an-hour on the water bath, the residue will be dry enough for weighing. The shallow cap is now removed and placed inside the dish, the perforated one, packed with asbestos, is substituted and a weighed beaker is placed underneath. Boiling ether or benzene is then poured into the dish, and after 50 c.c. has run through, all the fat will be extracted. L. DE K.

Estimation of Fat. By ERWIN VOIT [and OTTO KRUMMACHER] (*Zeit. Biol.*, 1897, 35, 555—582).—See this vol., ii, 175.

Analysis of Fats. The Gravimetric Bromine Method. By JULIUS LEWKOWITSCH (*J. Soc. Chem. Ind.*, 1896, 15, 859).—In consequence of the statement of Hehner (*Analyst*, 1895, 148) that the action of bromine on unsaturated fatty substances is complete and quantitative, the author has applied the gravimetric bromine method (Hehner, *Abstr.*, 1895, ii, 428) to a variety of oils, and from the bromine values thus found has calculated the corresponding iodine numbers. In the case of olive oil and rape oil, the numbers so obtained agreed closely with those of Hübl's method, but in all the other cases the discrepancy was very wide, and on that account the gravimetric bromine process is regarded as unfit for employment in fat analysis. M. J. S.

Bromine Absorption of Fats and Oils. By OTTO HEHNER (*J. Soc. Chem. Ind.*, 1897, 16, 87—89).—This paper is in part a reply to that of Lewkowitsch (preceding abstract). The author reproduces the table originally published in *The Analyst* (*Abstr.*, 1895, ii, 428) by which he showed that the amount of bromine absorbed by certain fats, as ascertained by the increase in weight, is in molecular proportion to the Hübl iodine number. The greatest discrepancy observed by Lewkowitsch was in the case of linseed oil, two specimens of which absorbed 18.68 and 10.4 per cent. of bromine, corresponding with 30.02 and 16.98 per cent. of iodine respectively, whereas the Hübl number for linseed oil ranges from 154 to 190. The author is unable to corroborate these low numbers, and refers to the experience of Williams (*Abstr.*, 1896, ii, 281); the latter, since the date of that publication, has further examined upwards of 200 samples of linseed

oil by the gravimetric bromine method, with results ranging from 110 to 120 per cent., but on two occasions has obtained low results (71·5 and 62·2) with specimens of apparent genuineness.

The bromination of a fat is accompanied by a considerable development of heat. If 1 gram of the fat, dissolved in 10 c.c. of chloroform, is treated with 1 c.c. of bromine, the rise of temperature, expressed in Centigrade degrees, gives, when multiplied by 5·5, a very close approximation to the Hübl number. The experiment is best made in a vacuum-jacketed tube.

M. J. S.

Hehner's Bromine Tests for Oils. By JOHN H. B. JENKINS (*J. Soc. Chem. Ind.*, 1897, 16, 193—195).—The author's experience of the gravimetric bromine absorption method and the bromothermal method corroborates that of Hehner, with linseed, as well as other oils. The results agree best, however, when the brominated oils are dried for 5 hours at 97°. At 125°, a continuous, though small, loss of weight occurs.

M. J. S.

Detection of Foreign Fats in Lard and Butter. By C. B. COCHRAN (*J. Amer. Chem. Soc.*, 1897, 19, 796—799).—Two c.c. of the melted lard or butter is introduced into a 25 c.c. graduated cylinder and dissolved by the aid of a gentle heat in 20 or 8 c.c. respectively of amyl alcohol (sp. gr. = 0·8159; boiling point, 129°). After cooling to 16—17°, the contents are kept at that temperature for two or three hours, and the deposit, which, if the lard is pure, should not exceed 4 c.c., is transferred to a small filter and the fusel oil drained off. The residue is then transferred to a test-tube and dissolved in ether, the tube plugged with cotton wool, and the ether allowed to slowly evaporate; the crystals which form are afterwards mounted in cotton-seed oil and microscopically examined. If the sample contains 10 per cent. of beef-fat, there will be no difficulty in recognising beef-stearin; with 20 per cent. of adulteration, lard-stearin will be practically absent.

L. DE K.

Estimation of Unsaponifiable Oil in Greases with a Lime Base. By HENRY BAILEY (*Chem. News*, 1897, 76, 174).—In the usual method, entailing complete saponification and extraction of the dried soap, the operations of drying and extraction are both unsatisfactory; they are obviated in the following method. Ten grams of the grease is completely decomposed by boiling and stirring with hydrochloric acid, and is then filtered, on a filter previously moistened with water, and washed free from hydrochloric acid with boiling water, any slight iridescence in the filtrate being ignored. The oils are heated and stirred with about 2 grams of strong potash and some alcohol, that is renewed from time to time, but when saponification is complete is nearly all evaporated away. The residue is warmed with about 100 c.c. of water until clear, and when cool is twice extracted with ether or light petroleum, using 30 c.c. the first and 20 c.c. the second time, a few drops of alcohol being added if the separation is not sharp. The combined extracts are evaporated in a tared wide mouthed flask and dried at a little above 100° until constant in weight.

D. A. L.

Estimation of Phenylhydrazine. By HENRI E. CAUSSE (*Compt. rend.*, 1897, 125, 712—714).—When phenylhydrazine is boiled with

arsenic acid in presence of acetic acid, it is completely decomposed, with formation of nitrogen, phenol and water, the arsenic acid being reduced. 198 grams of arsenious acid are formed for every 108 grams of phenylhydrazine oxidised.

About 0.2 gram of phenylhydrazine, free or in combination, is mixed with excess of a solution prepared by dissolving 125 grams of arsenic acid in a mixture of 450 grams of water and 150 grams of concentrated hydrochloric acid, filtering after cooling, and then diluting to 1000 c.c. with glacial acetic acid. The mixture is gently heated and finally boiled in a reflux apparatus. After about 40 minutes, the liquid is allowed to cool, made alkaline with sodium hydroxide solution, reacidified with hydrochloric acid, mixed with excess of sodium hydrogen carbonate and titrated with decinormal iodine solution.

The method is applicable to combinations of phenylhydrazine with aldehydes. If the aldehyde belongs to the benzene series, it has no influence on the result, but if it belongs to the acetic series it must first be removed.

Under certain conditions, phenylhydrazine forms a crystallisable compound with salicylic acid. C. H. B.

Testing Quinine. By MELCHIOR KUBLI (*Arch. Pharm.*, 1897, 235, 619—633. Compare *Abstr.*, 1896, ii, 550, and 1897, ii, 83, 168, 391).—Controversial. A reply to Hesse's remarks concerning the author's methods. A. W. C.

Analysis of Asphalt. By HERMANN ENDEMANN (*J. Soc. Chem. Ind.*, 1896, 15, 871—876; 1897, 16, 121—126).—From the researches of Boussingault, asphalt has hitherto been regarded as a mixture of a volatile hydrocarbon, petrolene, with a non-volatile substance, asphaltene, containing about 15 per cent. of oxygen, the asphaltene being the predominant constituent. More recently, the separation of these substances by means of solvents, especially light petroleum, has been employed for the purpose of analysing asphalt. The author shows that the results obtained by these methods may be entirely misleading. That portion of the asphalt which is insoluble in light petroleum, and is regarded as Boussingault's asphaltene, is, nevertheless, easily soluble in a mixture of petrolene with light petroleum, and is partially precipitated when the strong solution is diluted with petroleum, or with the weaker washings. As a consequence of this solubility, the proportion of petrolene in an asphalt is largely overstated when separation by solvents is attempted. On re-examining Boussingault's method of separating petrolene and asphaltene by heat, it was ascertained that the non-volatile portion absorbs a large amount of oxygen when heated in air; so that Boussingault's asphaltene is not really a constituent of natural asphalt, but is an oxidised product. This, and the fact that when this oxidised residue is dissolved in chloroform it is always accompanied by metallic oxides, induce the author to propose for it the name *asphaltic acid*, reserving the name asphaltene for that constituent of asphalt which remains when asphalt is heated at 250° in an atmosphere free from oxygen, and which has the empirical formula $C_{13}H_{18}O$. This asphaltene, which is entirely non-volatile, and is hard and brittle in the cold, fuses at 210°, and, when heated at 250° in air,

becomes covered with a wrinkled skin, increases in weight, and ultimately becomes hard and dry like sand, being converted into asphaltic acid. The latter is a black substance, which dissolves in soda, and is reprecipitated by acids. Although itself insoluble in chloroform, its compounds with metallic oxides seem to be soluble in a chloroform solution of asphaltene. It has the formula $C_{26}H_{26}O_4$, containing, therefore, the same percentage of oxygen as Boussingault's asphaltene. Its solution in sodium hydroxide readily absorbs oxygen, and this oxidised solution gives, with hydrochloric acid, a brown precipitate, which is a strongly acid substance of the formula $C_{26}H_{20}O_{12}$, for which the name *asphaltulmic acid* is suggested.

The soft and liquid asphalts known as malthas are hydrocarbons entirely free from oxygen, and containing a much larger proportion of volatile substances than the solid asphalts. A specimen was freed from petroleum by distillation in a vacuum. The residue was repeatedly washed with boiling alcohol, then dissolved in ether, and after removal of the ether was analysed. It is an inodorous, pale-coloured gum, with the formula $C_{26}H_{38}$. When heated in air, it is converted into asphaltic acid; the name *asphaltogen* is, therefore, adopted. It is solid at ordinary temperatures, but fuses below 100° , and is soluble in ether, whereas asphaltene is insoluble. As a practical application of the above facts, it is proposed that asphalts should be analysed by the following process: 5 grams of the asphalt is treated with chloroform, the insoluble matter is collected and treated in the usual manner, and the filtered chloroform solution is distilled from a weighed flask, the residue being dried for half an hour at 120° . A weighed quantity of this residue (0.2—0.3 gram) is then heated in a porcelain boat at 250° in a current of carbonic anhydride for 12 hours. The loss is reported as petroleum, the residue as asphaltene and ash. The results so obtained differ greatly from those of the treatment with solvents, but are far better adapted for controlling the practical applications of the material.

M. J. S.

Detection of Urobilin. By GEORGES DENIGÉS (*Chem. Centr.*, 1897, i, 1128; from *J. Pharm.*, [vi], 5, 395—397).—To prepare a dark-coloured urine for the spectroscopic detection of urobilin, 10 c.c. is mixed with 5 c.c. of mercuric sulphate solution, prepared from 5 grams of mercuric oxide, 20 c.c. of concentrated sulphuric acid, and 100 c.c. of water. An ammoniacal solution of urobilin gives a reddish colour with mercuric sulphate, and a violet colour with nickel and copper salts.

M. J. S.

Detection of Urobilin in Urine. By G. LEO (*Chem. Centr.*, 1897, i, 440; from *Boll. Chim. Farm.*, 1897, 36, 69—70).—The urobilin is precipitated with basic lead acetate, the precipitate washed first with water and then with a little absolute alcohol, and treated with alcoholic ammonia (10 c.c. of alcohol to 2 c.c. of aqueous ammonia). This extracts sufficient urobilin from the precipitate to give after concentration the characteristic fluorescence with ammoniacal zinc chloride.

M. J. S.

General and Physical Chemistry.

Relations between Molecular Structure and the Absorption Spectra of Colourless Organic Compounds. By WALTHER SPRING (*Rec. Trav. Chem.*, 1897, 16, 1—25).—Organic compounds generally regarded as colourless, have usually a pale blue tint when hydroxyl groups are present, this being the more marked the shorter the carbon chain, but in the absence of hydroxyl groups the colour inclines to yellow. Many of these compounds also give band absorption spectra, and 51 liquids were spectroscopically examined by means of a direct vision spectroscope the compounds including alcohols, acids, ethers, ethereal salts, aldehydes, nitro-compounds and hydrocarbons. The alcohols gave one band the position of which undoubtedly depends on the molecular structure, but the author does not find the simple direct relation to the molecular weight which was found by Russell and Lapraik (*Trans.*, 1881, 168). The acids also gave a spectrum with one band, but in the case of the ethers and ethereal salts, two bands were obtained which correspond closely in position with those of the related alcohols, or alcohol and acid, for example, ethylic acetate gave bands at 632 and 615 (arbitrary scale), whilst the bands of ethylic alcohol and acetic acid are at 633 and 615 respectively. In some cases, however, the juxtaposition of the bands causes coalescence, so that only one band results. The absorption band in benzene is in the same position as one of those present in benzoates, &c., and may be regarded as due to the phenyl group, but in toluene and xylene, &c., this band is displaced and approaches the position of the methyl band. Nitrobenzene and nitrotoluene do not give the multitude of bands characteristic of nitric peroxide, but have two bands only, one of which is peculiar to the phenyl derivatives, the other being probably indicative of the nitro-group.

L. M. J.

Photoelectric Properties of Salts previously Coloured by Heating in the Vapour of Alkali Metals. By JULIUS ELSTER and HANS GEITEL (*Ann. Phys. Chem.*, 1897, [ii], 62, 599—602).—It has been shown by Goldstein (*Abstr.*, 1895, ii, 150) that many salts become coloured under the influence of the cathodic discharge, and salts so coloured possess the peculiarity of readily losing negative electrification when subjected to the influence of bright light. A similar coloration of salts has been produced by Giesel (*Abstr.*, 1897, ii, 170) and Kreutz (*Abstr.*, 1897, ii, 210) by subjecting the salts to the action of sodium or potassium vapours, and the authors now show that salts so coloured exhibit the photoelectric peculiarity noticed in the case of those coloured by the cathodic discharge, as do also, but to a less extent, some naturally coloured varieties of rock salt. It hence appears probable that the coloration is due to a dilute solution of the metal in the solid salt, although it is noteworthy that Abegg found no indication of alkalinity in solutions of these coloured salts. The view of

Kreutz that the presence of iron salts is a cause of the coloration does not receive support.

L. M. J.

Change of the Zinc Sulphate in the Clark Cell. By WILHELM JAEGER (*Ann. Phys. Chem.*, 1897, [ii], 63, 354—365).—At 39°, the ordinary crystals of zinc sulphate, $\text{ZnSO}_4 + 7\text{H}_2\text{O}$, change into crystals of the composition $\text{ZnSO}_4 + 6\text{H}_2\text{O}$. There is a break in the solubility curve at this point, the solubility of the new salt being greater than that of the original compound. In keeping with this, the E. M. F. of the Clark cell shows a change at 39° on heating, and it is possible to cool the cell down again in such a way as to prevent a return of the zinc sulphate to the ordinary condition, abnormal values for the E. M. F. being thus obtained at ordinary temperatures. Two curves are thus obtained for the E. M. F. of the Clark cell. For the normal cell containing $\text{ZnSO}_4 + 7\text{H}_2\text{O}$

$$E_t = 1.400_5 - 0.00152(t - 39) - 0.000007(t - 39)^2.$$

For the abnormal cell containing $\text{ZnSO}_4 + 6\text{H}_2\text{O}$

$$E_t = 1.400_5 - 0.00102(t - 39) - 0.000004(t - 39)^2.$$

In using the Clark cell, care should therefore be taken not to raise the temperature above 40°, and to make certain that the zinc sulphate is present in its normal state.

H. C.

Theory of Galvanic Polarisation. By ANTON OBERBECK (*Ann. Phys. Chem.*, 1897, [ii], 63, 29—35).—The determination of galvanic polarisation in a closed circuit is regarded by Streintz as impossible (*Abstr.*, 1896, ii, 460), but the author would except from this generalisation polarisation due to very weak or to very strong currents. A mathematical treatment of the question is given.

H. C.

Electrosynthesis. By WILLIAM G. MIXTER (*Amer. J. Sci.*, 1897, [iv], 4, 51—62).—Mixtures which readily explode when subjected to an ordinary electric spark may not do so under the influence of the electric glow in an ozonising tube. Thus, oxygen and hydrogen in the ratio 1:2 at 235 mm. pressure did not explode, but combined slowly. Various explosive mixtures were therefore subjected to the glow discharge in eudiometer tubes and the rates of combination determined, but as no determinations of the current strength were taken, the relation between the rate of combination and the quantity of electricity discharged was not obtained. Hydrogen and oxygen were found to slowly combine, carbonic oxide and oxygen combined more rapidly, and even when perfectly dry combined slowly. Methane and oxygen combine in a manner consistent with complete combustion, but in the case of mixtures of acetylene with oxygen, ethylene with oxygen, and ethane with oxygen the quantity of the latter gas used is less than that required for complete combustion, whilst small quantities of the hydrocarbons were decomposed with the formation of acetylene. Very little ozone is formed during the discharge, and the oxidation cannot be due to its formation. The author does not consider the combination to be due to the union of ions, but to the interaction of the molecules themselves, which are made active by the glow discharge.

L. M. J.

Electrochemical Notes. By HANS JAHN (*Ann. Phys. Chem.* 1897, [ii], 63, 44—55).—Arrhenius (Abstr., 1893, ii, 441) has shown that when an alkali salt is electrolysed with a mercury cathode, a considerable time elapses from the beginning of the electrolysis before hydrogen makes its appearance. The explanation offered, that hydrogen is not a primary product of the electrolysis, but results from the action of the water of the solution on the alkali-metal amalgam primarily formed, has been called in question by Le Blanc (Abstr., 1894, ii, 225). As no direct proof of the formation of an alkali-metal amalgam in the process has been given, the author here shows by direct calorimetric measurements that such an amalgam must be formed during electrolysis with a mercury cathode.

A modification of the De la Rue cell is described in which the double salt, $\text{ZnCl}_2 \cdot 2\text{KCl}$, is used in place of zinc chloride alone. The formation of an insoluble basic salt is thus avoided. The E. M. F. of the cell in volts at the temperature t is given by the formula $E = 1.0136 - 0.000194t$.
H. C.

Electrolysis of Platinic Chloride. By FRIEDRICH KOHLRAUSCH (*Ann. Phys. Chem.*, 1897, [ii], 63, 423—430).—In the electrolysis of hydrogen platinochloride, H_2PtCl_6 , chlorine appears at the anode and platinum and hydrogen both appear at the cathode. It is, however, doubtful whether the platinum is a primary product of the electrolysis. The ordinary crystallised platinic chloride, $\text{PtCl}_4 + 5\text{H}_2\text{O}$, when dissolved in water and electrolysed, gave, with weak currents, hydrogen alone at the cathode, no platinum separating, and at the anode oxygen was obtained. With stronger currents, a deposit of platinum appears on the cathode and oxygen at the anode. The author regards the deposition of platinum in the last case as due to secondary action, and suggests that platinic chloride exists in solution as $\text{H}_2\text{PtCl}_4\text{O}$, with the ions H_2 and PtCl_4O . The secondary deposition of platinum may be due to the reaction $2\text{H}_2 + 3\text{H}_2\text{PtCl}_4\text{O} = \text{Pt} + 2\text{H}_2\text{PtCl}_6 + 3\text{H}_2\text{O}$ as the solution gradually changes to one of hydrogen platinochloride. The platinum cathode becomes bent during the passage of the current, perhaps owing to occlusion of the hydrogen taking place with contraction in volume.
H. C.

Electrolysis and Electrolytic Conductivity of certain substances dissolved in Liquid Ammonia. By HAMILTON P. CADY (*J. Physical Chem.*, 1897, 1, 707—713).—The dissociative power of liquid ammonia on dissolved substances has been tested by determining the electrolytic conductivity of the solutions. Ordinary commercial liquid ammonia was used, its determined conductivity being 71×10^{-7} . The presence of a small amount of water does not seem to have a measurable effect on either the conductivity of ammonia alone, or of solutions of substances dissolved therein. When a small quantity of a soluble salt is added to the ammonia, the solution becomes an excellent conductor. In the case of sodium or potassium salts, the solution turns blue during electrolysis, but becomes colourless again when the current is shut off. When a current is passed through a solution of an ammonium salt in ammonia, there is a violent evolution of gas but no signs of a blue coloration. In neither of

these experiments could any evidence be detected of a blue coloration that might be ascribed to the presence of free ammonium. When a current is passed through solutions of salts of silver, copper, or barium, the metals are deposited on the cathode, but there is no sign of a blue colour. A solution of sodium in ammonia is of a bright blue colour, and is an excellent conductor. There is no deposit on the electrodes, no gas is evolved, and the blue colour is not altered by the passage of an enormous quantity of electricity. If only a little sodium is present, the colour becomes more intense round the cathode. There is no polarisation current.

Whilst regarding his results as preliminary, the author concludes that ammonia seems to possess the power of dissociation of dissolved substances to as great an extent as water, and in most cases the ions seem to travel even faster in it than in water. The work is to be continued.

H. C.

Conductivity of Solutions of some Salts in Pyridine. By ST. VON LASZCZYNSKI and STANISLAUS VON GORSKI (*Zeit. Elektrochem.*, 1897, 4, 290—293).—The electrolytic conductivities at 18° of solutions of potassium, sodium, and ammonium iodides and thiocyanates and of lithium chloride in pyridine were investigated. The conductivity of the pyridine itself was inappreciable. The molecular conductivity increases more rapidly with increasing dilution than is the case with aqueous solutions, the rate of increase passing through a maximum value. A similar peculiarity has been observed in the case of other organic solvents, in isolated instances also with water. In accordance with Carrara's view, the authors consider the maximum to indicate a maximum dissociating power of the solvent. Lithium chloride solutions in pyridine have a remarkably low conductivity; this may be due to the formation of the salt $\text{LiCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ which has been isolated in the crystalline condition.

Metallic sodium has little or no action on pyridine, but attempts to prepare alkali metals by electrolysis of solutions of their salts in pyridine were not encouraging. A blackish crust containing metallic lithium was obtained from a solution of the chloride, and a yellowish grey crust, containing a little potassium, from a solution of potassium thiocyanate, but the metal acts on the dissolved salt, forming sulphide. An attempt to prepare ammonium amalgam by electrolysis of a pyridine solution of ammonium thiocyanate gave no definite result, whilst solutions of magnesium, cerium, and cobalt chlorides and of silver iodide were found to be non-conductors.

T. E.

Ionic Reactions and their Significance in Electrochemistry. By FRIEDRICH W. KÜSTER (*Zeit. Elektrochem.*, 1897, 4, 105—113).—A lecture, dealing more especially with the bearing of the ionic hypothesis on analytical chemistry, in which the following lecture experiments are described.

In order to show the electrical exchange represented by the equation $\text{Cu}^{++} + \text{Fe} = \text{Cu} + \text{Fe}^{++}$, pieces of iron and copper are immersed in a solution of sodium sulphate, the former near the top, the latter near the bottom of the vessel; a few crystals of copper sulphate being brought into the liquid near the copper, a current at once flows from

the copper to the iron through the external circuit. The change, $2\text{Fe}^{+++} + \text{Fe} = 3\text{Fe}^{++}$, is similarly illustrated by using two iron plates in a solution of common salt and placing some ferric chloride near the lower one.

The electrical exchanges connected with the reversible reaction, $\text{Fe}^{++} + \text{I} = \text{Fe}^{+++} + \text{I}^-$, are shown by means of two platinum electrodes standing in small crystallising dishes which are placed in a larger dish; the latter is filled with a solution of potassium chloride and, under it, some iodine is placed in the one small dish and a strong solution of ferrous chloride in the other; the current then flows (in the external circuit) from the iodine to the ferrous solution, but by increasing the concentration of the iodine ions or of the ferric ions the reaction, and with it the direction of the current, is reversed. The change, $\text{I}^- + \text{Br} = \text{Br}^- + \text{I}$, is demonstrated in a similar manner. If electrodes of iron and platinum respectively are immersed in a solution of potassium chloride, and a little iodine added in the vicinity of the platinum, a current is developed owing to the reaction $\text{Fe} + 2\text{I} = \text{Fe}^{++} + 2\text{I}^-$.

A saturated solution of hydrogen chloride in toluene does not conduct electricity, even under a pressure of 72 volts; nor does it act on calcium carbonate, but the addition of a little water enables it to do both the one and the other. A saturated (about 0.1 normal) solution of carbonic acid colours methyl-orange less intensely red than a 0.01 normal solution of acetic acid owing to the difference in their dissociation. The diminution of dissociation produced by increasing the concentration of one ion is shown by adding a trace of sodium hydrogen carbonate to the carbonic acid, whereon the red colour disappears, or of sodium acetate to the acetic acid solution. No change of colour is produced by adding sodium chloride to a weak solution of hydrochloric acid coloured by methyl-orange. Another phenomenon of a similar kind is the precipitation of lead chloride from its saturated solution by the addition of a solution of common salt.

The presence of copper in the form of a cation in a solution of copper sulphate, and in the form of a complex anion in Fehling's solution, is proved by passing a current through two U-tubes, one of which contains a solution of cupric sulphate on the surface of which a solution of sodium sulphate floats whilst the other is similarly filled with Fehling's solution and an alkaline solution of Rochelle salt. The blue zone in the one tube moves in the same direction as, in the other tube in the opposite direction to, the current. The absence of cupric ions from Fehling's solution is further shown by means of a galvanic cell containing lead and copper immersed respectively in solutions of lead acetate and copper sulphate; in this combination, lead dissolves and copper is precipitated, but both the reaction and the direction of the current are reversed when an alkaline solution of Rochelle salt is added to the cupric sulphate solution.

T. E.

Determination of the Expansion of Water between 0° and 40°. By PIERRE CHAPPUIS (*Ann. Phys. Chem.*, 1897, [ii], 63, 202—208).—The expansion of water between 0° and 40° was measured, a platinoiridium dilatometer being used. A table is given of the

densities, referred to the maximum density as unity, these numbers varying only slightly in the sixth decimal place from those given by Thiesen, Scheel, and Diesselhorst (Abstr., 1897, ii, 307). H. C.

New Form of Constant Volume Air Thermometer. By J. R. ERSKINE MURRAY (*J. Physical Chem.*, 1897, 1, 714—717).—A constant volume air thermometer is described in which the total pressure of the enclosed air, and hence its temperature, is measured directly by the height of one column of mercury. The external atmospheric pressure is eliminated by the adjustment of an auxiliary reservoir of mercury.

H. C.

Experimental Determination of the Hydrothermal Value of a Bomb Calorimeter. By HARVEY W. WILEY and W. D. BIGELOW (*J. Amer. Chem. Soc.*, 1897, 19, 439—451).—The authors describe the direct experimental determinations of the water equivalent of a bomb calorimeter by the addition of warm water to the calorimeter immersed in cold water. The temperature of the warmer water was only about 10 degrees above that of the cold water, but temperatures were read to 0.001° by means of Beckmann thermometers. The various necessary precautions are noted, and the values obtained directly were 406.6, 407.4, 398.1, and 410.3, the value calculated from the weights and specific heats of the various parts being 410.6. The Regnault-Pfaundler correction for the cooling effect of the surrounding atmosphere is, in the authors' opinion, practically unnecessary.

L. M. J.

Heat of Neutralisation of Glycerophosphoric Acid. By H. IMBERT and G. BELUGOU (*Compt. rend.*, 1897, 125, 1040—1042).—The neutralisation of glycerophosphoric acid by sodium hydroxide develops +14.95 Cal. for the first equivalent, 13.75 Cal. for the second equivalent, and +0.1 Cal. for the third equivalent. With potassium hydroxide, the values are +15.9, +13.9, and +0.4 Cal. respectively. The values for the first and second equivalents are practically identical with those obtained with phosphoric acid. The fact that there is practically no thermal disturbance on adding a third equivalent of alkali shows that the group, $\text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, has displaced the hydroxyl group with the alcoholic function.

C. H. B.

Heat of Dissociation of Molecules of Elements. By WILHELM VAUBEL (*J. pr. Chem.*, 1897, [ii], 55, 542—547).—The difference between the heats of formation of $2\text{Cu}_2\text{O}$ and 2CuO is 72 Cal., and on the assumption that the actual heat evolved by the union with the same quantity of oxygen is the same for cuprous and cupric salts, this value, 72 Cal., is the heat required to effect the separation of the copper atoms. The value similarly obtained for mercury is 228 Cal., and these two values are in the same ratio as the atomic weights of the two

elements. Since, however, the separation is only for $\begin{array}{c} \text{Cu} - \text{Cu} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$, and not

for $\text{Cu} = \text{Cu}$, the actual values for the dissociation heat are double the above values, that is, 144 and 456 Cal., in which case the proportionality to the atomic weight extends also to iodine, the heat of dissociation of which was found by Boltzmann to be 285 Cal. The heat of

dissociation of nitric peroxide is hence calculated as 104.9 Cal., whilst the value deduced by Berthelot and Ogier was 106 Cal.; that of hydrogen must hence be very small, and this result is in accord with Jahn's observations (Abstr., 1896, ii, 230). Similar calculations deduced from the thermal relations of the chlorides do not lead to concordant results, but in this case the fundamental assumption probably does not hold.

L. M. J.

Some Boiling Point Determinations. By H. J. STEUBER (*J. Physical Chem.*, 1897, 1, 643—646).—A determination of the boiling points of solutions containing alcohol, salt, and water shows that the presence of alcohol increases the apparent reacting weight of the salt. A similar increase is observed if sugar is substituted for salt.

H. C.

Solubility and Boiling Point. By OLIVER W. BROWN (*J. Physical Chem.*, 1897, 1, 784—786).—Steuber (preceding abstract) has shown that when salt or sugar is added to aqueous alcohol the boiling point does not rise as much as when pure water is taken. A natural conclusion is that the disturbing influence of the alcohol would be less if the substance added were soluble both in alcohol and water. Experiments with carbamide confirm this view.

H. C.

Vapour Pressure of Dilute Aqueous Solutions at 0°. By KONRAD DIETERICI (*Ann. Phys. Chem.*, 1897, [ii], 62, 616—643).—Since the freezing point of a solution is not accurately a linear function of the osmotic pressure (Abstr., 1894, ii, 343), the author has determined directly the vapour pressure of a number of dilute solutions. The apparatus employed has been previously described (*Ann. Phys. Chem.*, [ii], 50, 47), and depends essentially on the motion of a membrane subjected, on one side, to the vapour pressure of the solution, and, on the other, to that of pure water; the motion of the membrane is communicated to a mirror and hence to a scale, the scale readings being calibrated by the use of a solution of known vapour pressure. Dilute solutions of phosphoric acid, sulphuric acid, sodium chloride, calcium chloride, cane-sugar, dextrose, and carbamide were examined at various dilutions, and the molecular lowering calculated at each dilution. In the case of sulphuric acid solutions, the molecular reduction of the vapour pressure *decreases* with increasing dilution, and appears to reach a minimum for a N/10 solution, a result in accord with the observations of Ponsot (Abstr., 1896, ii, 412) and of Loomis (Abstr., 1896, ii, 352). Similar results were obtained with phosphoric acid and calcium chloride solutions, but for sodium chloride the molecular reduction remains constant between the dilutions N/1 and N/10. For all the electrolytes, therefore, the effect of dilution is the reverse of that predicted by the dissociation theory. The experiments with solutions of cane-sugar, dextrose, and carbamide lead to analogous results, the author's determinations agreeing with those of Loomis in so far that very dilute solutions gave a value lower than the normal value, whilst the results further indicate that the molecular reduction of the vapour pressure is dependent on the nature of the dissolved substance.

L. M. J.

Vapour Pressure of Reciprocally Soluble Liquids. By WILHELM OSTWALD (*Ann. Phys. Chem.*, 1897, [ii], 63, 336—341).—The question whether two liquids are completely or only partially miscible with one another is generally one of temperature. As all vapours are completely miscible down to the critical temperature, liquids must be completely miscible at this temperature; but below this temperature a separation may take place. The existence of a "critical solution temperature" at which this first occurs has been indicated by Masson (*Abstr.*, 1891, 791). At the critical solution temperature, the two saturated solutions which the liquids form have the same composition, the same vapour pressure, and therefore also vapours of identical composition. The composition of the liquid therefore, at this point, must be the same as that of the vapour which it emits on boiling. The author shows that below this point the composition of the distillate obtained from a mixture of two partially miscible liquids, may be also considered as that of a liquid mixture which, if homogeneous, would have the same composition as its vapour.

H. C.

Vapour Tensions, Freezing and Boiling Points of Ternary Mixtures. By W. LASH MILLER (*J. Physical Chem.*, 1897, 1, 633—642).—A theoretical paper dealing with one of the functions introduced by Gibbs in his "Equilibrium in Heterogeneous Systems."

H. C.

Vapour Pressures of Hydrated Salts which remain transparent on Efflorescence. By GUSTAV TAMMANN (*Ann. Phys. Chem.*, 1897, [ii], 63, 16—22).—If a crystal loses water without losing its transparency, it may be regarded as forming a system composed of a solid and a gaseous phase which is not in complete equilibrium, the number of phases being only equal to the number of substances present, and the vapour pressure will therefore depend on the amount of water which has been removed from the solid phase. Measurements are given of the water lost by the minerals heulandite, chabazite, and desmine (stilbite) when exposed over sulphuric acid solutions of varying concentrations, and it is shown that the vapour pressure varies with the amount of water lost.

H. C.

Vapour Pressure Method of determining Molecular Weights. By WILLIAM R. ORNDORFF and H. G. CARELL (*J. Physical Chem.*, 1897, 1, 753—759).—The authors employ a method similar to that used by Will and Bredig (*Abstr.*, 1889, 820) for the determination of the molecular weights of a number of compounds in alcoholic solution. The rate at which the air passes through the apparatus is found to influence the results. Phenol gave numbers rather lower than the theoretical, but in the other cases examined a fair agreement was obtained.

H. C.

Cryoscopic Experiments with the Acetyl Derivatives of the Etheral Tartrates. By EMANUELE PATERNO and C. MANUELLI (*Real. Accad. Linc.*, 1897, [v], 6, i, 401—405).—The authors have made determinations of the molecular depression of the freezing point of diethylic diacetyldextrotartrate by toluene, paraxylene, naphthalene, nitrobenzene, ethylic oxalate, and diethylic monoacetylmaleate; the

mean molecular depression thus obtained is 133.2. The racemic isomeride gives about one-half the normal depression, using the dextro-tartrate as solvent; if the racemate is dissociated in the solution, the molecular depression is due to the molecules of the levotartrate only. The racemate is dissociated in freezing benzene. W. J. P.

Use of Methylic Oxalate in Cryoscopy. By G. AMPOLA and C. RIMATORI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 404—407).—Determinations of the molecular depression of the freezing point of methylic oxalate by toluene, ethylic oxalate, bromoform, paraxylene, nitrobenzene, veratrole, phenol, thymol, trimethylcarbinol, caprylic alcohol, isobutyric acid, valeric acid, and the diethylic ether of glycerol show that, as a solvent in cryoscopic work, methylic oxalate behaves somewhat differently from veratrole; in methylic oxalate, the alcohols and acids give abnormally low molecular depressions, which decrease as the concentration increases. The mean molecular depression of the freezing point of methylic oxalate is 52.87. W. J. P.

Relations between the Molecular Weights and Densities of Liquids and Solids. By Ugo ALVISI (*Real. Accad. Linc.*, 1897, [v], 6, i, 77—85. Compare Abstr., 1895, ii, 307).—From the consideration of a large number of tabulated data, the author concludes that the molecular volumes of the oxides of the composition R_2O is twice that of those of the oxides RO of the same metal; R may be either Pb , Hg , or Cu . Relations may also be formulated between the molecular volumes V of the oxides of metals in adjoining vertical columns of Mendeléeff's periodic classification; these are of similar form to V of CaO/V of $SrO = V$ of K_2O/V of Rb_2O . Many relations of this type are quoted, and the principle is enunciated that equal volumes contain equal numbers of equivalent weights of matter; this is well illustrated by a table showing the molecular and equivalent volumes of the organo-metallic derivatives. There is, in many cases, considerable deviation from the law, owing to the conditions not being comparable. Tables are given showing the volume constants of the oxides and sulphates, and of salts of the composition MRO_3 , M_2RO_3 , and M_3RO_3 . W. J. P.

Relation of the Taste of Acids to their Degree of Dissociation. By THEODORE W. RICHARDS (*Amer. Chem. J.*, 1898, 20, 121—126).—The sour taste of acids is attributed to the hydrogen ions liberated in their aqueous solutions. This view is supported by the fact that a solution of hydrochloric acid, of distinctly sour taste, becomes tasteless when neutralised with potash. From this, the author also concludes that potassium and chlorine ions possess much weaker taste than hydrogen ions. Dilute solutions of less ionised acids, for example, acetic and tartaric acids, are not so sour to the taste as corresponding solutions of the mineral acids. The addition of small quantities of sodium acetate to dilute solutions of hydrochloric and acetic acid diminishes their taste to a marked extent. This is in accordance with the view that the almost wholly dissociated sodium acetate is capable of destroying the freedom of the hydrogen ions.

The author finds that the end-point of a reaction between decinormal

solutions of acid and alkali can be detected by the sense of taste to within 0.5 per cent.

W. A. D.

Direct Measurement of Osmotic Pressure. By ANDREA NACCARI (*Real. Accad. Linc.*, 1897, [v], 6, i, 32—37).—The author has examined the osmotic pressure law, using for the osmometer a porous pot washed with potash, water, hydrochloric acid, and lastly water; the membrane is formed by placing the pot in 3 per cent. copper sulphate solution and after removing the solution and superficially washing, introducing a 3 per cent. potassium ferrocyanide solution into the pot.

Using such a vessel with solutions of glucose, mannitol, salicin, and antipyrine, a fairly good correspondence was obtained between the observed and calculated values of the osmotic pressures. Glycerol solutions set up a low osmotic pressure, owing apparently to the permeability of the membrane to glycerol; unsatisfactory results were also obtained with phenol.

W. J. P.

Osmotic Pressure and Electrolytic Dissociation. By ISIDOR TRAUBE (*Ber.*, 1898, 31, 154—159. Compare Abstr., 1895, ii, 308).—The author has previously arrived at the conclusion that the contraction which occurs when a substance is dissolved in water is proportional to the concentration of the solution and is almost independent of the nature of the dissolved substance. The contraction is about 13.5 c.c. for every dissolved gram-molecule of a non-electrolyte or for every dissolved gram ion of an electrolyte. It is thought that the contraction in aqueous solutions is due to the strong attraction between the solvent and the dissolved substance, and this leads to the hypothesis of union (changing union) between the water and the dissolved substance. The number of water particles (α) with which a given molecule of a substance in dilute solution combines, is equal for all non-electrolytes, and for dissolved electrolytes increases proportionally to the number of ions. From this, Van't Hoff's conclusion, that the osmotic pressure of a solution is equal to the pressure which the dissolved substance in the form of a gas would exert at that temperature, may be deduced.

In this deduction, use is made of the hypothesis that a molecule of any non-electrolyte in any dilute solution at any given moment is in union with only one particle of the solvent. The author proceeds to show that his views and those of Poynting are more in accord with observed facts than are the usual views of osmotic pressure. Explanations are given for the following facts: (1) Molecular weights as determined in different solvents vary, (2) colloidal substances have an osmotic pressure = 0 or nearly 0, (3) the course of any given reaction depends largely on the nature of the solvent employed (Menschutkin), (4) inversion of sugar and similar processes.

The hypothesis of electrolytic dissociation, according to Arrhenius, is considered quite superfluous. The author's view is that in dilute solutions of, say, sodium chloride, one molecule of sodium chloride is united to two of water, in concentrated solutions to one of water.

J. J. S.

[Osmotic Pressure and Electrolytic Dissociation.] By ISIDOR TRAUBE (*Ber.*, 1898, 31, 160—162).—A reply to Jahn's criticisms (this vol., ii, 153).

Absorption of Gases in Liquids at Various Temperatures. By CHRISTIAN BOHR (*Ann. Phys. Chem.*, 1897, [ii], 62, 644—651).—The relation between the absorption coefficient and temperature is given by the equation $a(T - n) = k$, where a is the absorption coefficient, T the absolute temperature, and n and k constants for each gas,* and this form of expression is found to give good agreement with the observed values in the cases of hydrogen, oxygen, nitrogen, carbonic oxide, carbonic anhydride, nitric oxide, and ethylene, in water, and of carbonic anhydride, nitric oxide, nitrous oxide, methane, and ethylene, in alcohol. The expression is tested to 45° in the case of the first four gases; for the rest, it is tested only to 26°, and above these temperatures graphical construction shows that aT is no longer a linear function of a , that is, the expression is no longer valid. For the aqueous solutions, the value of n appears to be a function of the molecular weight of the dissolved gas, being given by the equation $\sqrt{M} = 0.04968n - 6.286$.

L. M. J.

Influence of the Solvent on Ionic Velocities. By CARLO CATTANEO (*Real. Accad. Linc.*, 1896, [v], 5, ii, 207—214).—The author has determined the ionic velocities of chlorine in sodium and ammonium chlorides in aqueous and glycerol solutions at 20—25°. For sodium chloride, the mean ionic velocities of the chlorine in water and glycerol are 0.658 and 0.645 respectively, the corresponding values for ammonium chloride being 0.510 and 0.568; the values for sodium chloride are less in mixtures of water and glycerol than in either of these solvents separately, λ being the molecular conductivity, $10^8\lambda$ were found to be 1020 and 4.03 for sodium chloride in water and glycerol respectively, whilst for ammonium chloride the values 1200 and 5.20 were respectively obtained.

W. J. P.

Ionic Velocity of Chlorine in Hydrogen Chloride Dissolved in Various Solvents. By CARLO CATTANEO (*Real. Accad. Linc.*, 1897, [v], 6, i, 279—286).—The author has determined the ionic velocity of chlorine in hydrogen chloride dissolved in water, ethylic alcohol, methylic alcohol, amylic alcohol, glycerol, ether, and chloroform, and gives the numerical results in tabular form; the velocity constant has practically the same value, namely, 0.21 in water, ethylic alcohol, ether, and solutions of hydrogen chloride in chloroform, whilst a slightly higher value, namely, 0.24, is obtained in methylic and amylic alcohols and glycerol.

W. J. P.

Formation and Transformation of Hylotropic-isomeric Forms of Compounds. By KARL SCHAU (Ber., 1898, 31, 126—129).—The author applies the term hylotropic-isomeric to such forms of compounds as can change directly into other forms, examples being cyanic and cyanuric acids, rhombic and monosymmetric sulphur, &c. The physical, as distinguished from the chemical, isomerism of crystallised substances is characterised by the power to change directly into

* It may be noticed that the expression given simplifies to $a_t = a_0/(1 + kt)$.

a different form in the absence of any solvent; when no such change can be effected, the case is to be considered one of tautomerism, even in the absence of direct chemical evidence. Thus the two forms of metanitracetotoluidide described by Gattermann yield solutions which are identical in properties, but cannot be made to pass directly from one form to the other, and hence must be considered as tautomeric.

The author's experiments with benzophenone, which will be subsequently described, lead him to suppose, in opposition to Ostwald's view (*Abstr.*, 1897, ii, 308), that some substances in the "metastabile" state can be converted into a more stable form in the absence of crystals of the substance, by means the exact nature of which has not yet been ascertained.

A. H.

Accidental Causes of Non-reversibility in Chemical Changes.

By ALBERT COLSON (*Compt. rend.*, 1897, 125, 945—947).—When phosphoric acid is displaced from normal sodium phosphate by dry hydrogen chloride, considerably more than half the phosphoric acid is converted into pyrophosphoric acid. One of the factors in the inverse change is thereby destroyed, and the reaction becomes non-reversible. In the action of hydrogen sulphide on silver sulphate, the liberated sulphuric acid interacts with the remaining hydrogen sulphide, water and sulphurous anhydride being formed, and consequently this reaction also is non-reversible, even when the temperature has not exceeded 10°.

C. H. B.

Explosion Figures. By JOHANNES PINNOW (*J. pr. Chem.*, 1897, [ii], 56, 520—521).—When a mixture of hydrogen and oxygen gases is exploded in tubes which have been dusted with lycopodium powder and then allowed to remain for several days, the water is deposited in rings; on warming the tube, the rings disappear, but are re-formed in part as the tube cools, and precisely at the original places. Their position can be fixed by passing in silicon fluoride, and the deposits so obtained can be photographed. The distance between the rings varied from 2.8 to 4.2 mm. as the diameter of the tube varied from 1.4 to 2.0 cm., being greater as the diameter is greater; the length of the tubes varied from 12.6 to 19 cm.

C. F. B.

Two Liquid Phases. By WILDER D. BANCROFT (*J. Physical Chem.*, 1897, 1, 647—668).—In continuing a discussion of the cases dealt with in a former paper (this vol., ii, 65), the author gives a graphical representation of the equilibria in three-component systems when one pair, two pairs, and three pairs of the components can form two liquid phases.

H. C.

Ternary Mixtures. By WILDER D. BANCROFT (*J. Physical Chem.*, 1897, 1, 760—765).—With two partially miscible liquids and a third consolute with the other two, it is always possible to prepare a series of solutions any one of which will cloud on addition of a drop of either of the two partially miscible liquids. On the triangular diagram (this vol., ii, 65) is given the general form of the isotherm for a system composed of two partially miscible liquids, and a third miscible in all proportions with the other two, and it is shown how phenomena such as the above can then be deduced.

H. C.

Precipitation of Salts. By A. ERNEST TAYLOR (*J. Physical Chem.*, 1897, 1, 718—733).—In continuing the work of Bathrick (*Abstr.*, 1897, ii, 135) on the precipitation of salts from aqueous solutions by alcohol and acetone, further confirmation of the previous results was obtained. To ternary mixtures of this type, equations of the general form $(x + A)y^n = C$ and $(x + A)(y + B)^n = C$ apply. The constant n is independent of the temperature, but varies with the precipitating agent. A and B vary with the temperature, and are each characteristic of one of the non-miscible substances, A being a function of y and B of x .
H. C.

Fourth Annual Report of the Committee on Atomic Weights. By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1897, 19, 359—369).—A review of the work done on atomic weight determinations during 1896, including a table of values representing the results obtained by combining all the best data.
A. W. C.

Molecular Weights of some Carbon Compounds in Solution. By CLARENCE L. SPEYERS (*J. Physical Chem.*, 1897, 1, 766—783).—The molecular weights of a number of carbon compounds were determined by the boiling point method, a modified form of the apparatus devised by Orndorff and Cameron (*Abstr.*, 1895, ii, 480) being used. The solvents employed were water, methylic, ethylic, and propylic alcohols, chloroform, and toluene. The results are given in tabular form.
H. C.

Molecular Weights of Solid Substances. By ISIDOR TRAUBE (*Ber.*, 1898, 31, 130—137. Compare *Abstr.*, 1897, ii, 478).—By a comparison of the specific gravities of a number of solid organic substances (as determined by Schröder), the author is able to show that the volume of the group CH_2 is practically the same in solid as in liquid compounds; the extreme variations being, however, +20 and -14 per cent. of the mean value. Assuming that this also holds good for the atomic volumes of the elements, it is possible to calculate the co-volumes for a number of solid substances, the result being that the co-volume for the solid state appears to have about half the value which it possesses for liquids. Since a diminution of the co-volume on solidification can only be due to the association of molecules, the author assumes that the co-volume for the solid state is in reality equal to that for the liquid state, and that Avogadro's law holds for the solid state. Hence he is able to calculate the association factor for the compounds in question, and finds that it is roughly equal to 2, all these compounds being therefore bimolecular in the solid form. This conclusion is confirmed by a comparison of a number of inactive racemic compounds, which are undoubtedly bimolecular, with the corresponding active components, the latter are found to have the same co-volumes, and therefore must also be bimolecular. An application of the same method to inorganic salts shows that those which yield two ions are bimolecular, whereas those which yield three ions are monomolecular.

The author adduces Küster's experiment on naphthol and naphthalene in favour of his views, as well as the fact that a large number of

solid compounds have vapour densities at low temperatures which correspond with a molecular weight double that which they possess at high temperatures.

A. H.

Constitution of Inorganic Compounds. VII. The Molecular Weights of Inorganic Salts. By ALFRED WERNER (and in part P. FERCHLAND, A. MAIBORN, W. SCHMUJLOW, and M. STEPHANI) (*Zeit. anorg. Chem.*, 1897, 15, 1—41).—The molecular weights of a number of inorganic salts were determined by the rise of the boiling point of an organic solvent in which little or no dissociation would be expected to occur. It was found that many nitrogen and sulphur compounds are very suitable solvents, and piperidine, pyridine, benzonitrile, methylic sulphide, and ethylic sulphide were so employed, the inorganic salts examined being chiefly the halogen salts of silver, cadmium, tin, copper, mercury, lead, iron, zinc, cobalt, nickel, and aluminium. Many of the salts were found to form additive compounds with piperidine, and similar combinations occur in a few other cases such as lead nitrate with pyridine, cuprous chloride or cadmium iodide with methylic sulphide, and mercuric iodide with ethylic sulphide. The molecular constant for each solvent was obtained by means of solutions of anthracene and diphenylamine with the following results: methylic sulphide, 18·5; ethylic sulphide, 32·3; pyridine, 30·07; piperidine, 28·4; benzonitrile, 36·55. Most of the salts examined gave results corresponding with a simple normal molecular weight. Aluminium chloride gave elevations corresponding with AlCl_3 , analogous results obtaining for ferric chloride. Cobaltous chloride and bromide, stannous chloride and bromide, and lead nitrate are all monomolecular, that is, contain bivalent metallic atoms. Remarkable results were, however, found in the case of the cuprous salts, as cuprous bromide gave, in ethylic sulphide, the elevation corresponding with the molecular weight 226, but in methylic sulphide and pyridine that corresponding with the value 140 ($\text{CuBr} = 143$), whilst cuprous chloride gave the molecular weight 120 in all solvents, and cuprous cyanide gave the value corresponding with $\text{Cu}_2(\text{CN})_2$. It hence appears that the normal molecules of the cuprous salts are represented by the simple formulæ CuCl , &c., with partial association to Cu_2Cl_2 , but as the result may be also explained by dissociation of the more complex molecules, conductivity determinations were also made, and these indicated the absence of metallic ions ($\mu = 0\cdot05$). A similar tendency to polymerise was observed in the case of the silver haloids, which gave elevations corresponding with double and treble molecules, a result which the author considers is a further confirmation of his views regarding the constitution of the cuprous salts.

L. M. J.

Inorganic Chemistry.

Effect of Light on the Combination of Hydrogen and Bromine. By J. H. KASTLE and W. A. BEATTY (*Amer. Chem. J.*, 1898, 20, 159—163).—When glass bulbs, filled with a mixture of hydrogen

and bromine, and heated to 196° in the vapour of boiling ortho-toluidine, are exposed to direct sunlight, a rapid combination of the elements takes place, the amount of change being proportional to the time of exposure to light. When the bulbs are heated to the same temperature in the dark, little or no action occurs. The hydrogen used in all the authors' experiments, although in several cases carefully purified, was not freed at all from moisture. W. A. D.

Dissociation and Polymerisation of Gases and Vapours; Dissociation of Chlorine at High Temperatures. By ANATOLE LEDUC (*Compt. rend.*, 1897, 125, 937—939).—The author compares the densities of chlorine between 0° and 1400° as calculated by his method (this vol., ii, 108) with the observations of Friedel and Crafts, Jahn, Crafts, and V. Meyer. The numbers show that there is no appreciable dissociation up to 440° , and Meyer's numbers, which are not very concordant, indicate that there is no dissociation at 900° and 1200° . The only evidence of dissociation is the number 2.02 (Calc. 2.4483) observed by Crafts at 1400° , and this is an isolated observation. C. H. B.

Electrolysis of Hydrochloric Acid. By FRITZ HABER and S. GRINBERG (*Zeit. anorg. Chem.*, 1898, 16, 198—228).—The original paper contains a full discussion of the theoretical bearing of the results obtained by the authors. In concentrated hydrochloric acid, chlorine is formed at the anode in theoretical quantity, the amount decreasing as the acid is diluted, until only a small percentage is produced. Traces of hypochlorous acid are found at the anode in the electrolysis of dilute acid. Chloric acid amounting to one-third of the quantity which can be theoretically produced by the current employed is found in solutions varying from normal to N/30, small quantities of hydrogen peroxide accompanying the chloric acid. Perchloric acid is formed in dilute acid to an amount corresponding with one-fourth of that theoretically possible from the current employed. Oxygen is evolved at the anode; in dilute acids, the oxygen evolved constitutes 50 per cent. of the gas from the anode. E. C. R.

Oxygen at Low Pressures. By RICHARD THRELFALL and FLORENCE MARTIN (*Chem. News*, 1897, 76, 283—284).—Oxygen under a pressure of 0.25 mm. of mercury was caused to bubble through a solution of starch and potassium iodide in glycerol at the rate of 20 bubbles a minute, and altogether for $17\frac{1}{2}$ hours, but no visible effect was produced, although when electrically ozonised 20 bubbles of the same oxygen produced a faint yellow colour. Hence the peculiar behaviour of oxygen at low pressures does not seem to be due to the formation of ozone. D. A. L.

Combustion in Rarefied Air. By A. BENEDICENTI (*Real. Accad. Linc.*, 1896, [v], 5, i, 404—410).—With the object of elucidating the question of combustion at high altitudes, the author has made experiments on the burning of a lamp fed with olive oil under various atmospheric pressures. He finds that combustion is just as complete under 360 mm. pressure, corresponding to an altitude of 6000 metres, as at ordinary pressures, the only difference being that the speed of

combustion is less at the lower pressure; no appreciable increase occurs in the quantity of carbonic oxide produced as the pressure diminishes.

W. J. P.

Behaviour of Sodium Thiosulphate Solutions with Acids.

By GEORG AARLAND (*Chem. Centr.*, 1897, i, 677; from *Phot. Arch.*, 38, 17—20).—The author finds that when a solution of sulphurous acid is added to a solution of sodium thiosulphate, no decomposition takes place, although the mixture is strongly acid, and with zinc evolves hydrogen. Moreover, such a mixture may be boiled with dilute sulphuric acid without causing any precipitation of sulphur.

E. W. W.

Nitrohydroxylamic Acid. By ANGELO ANGELI (*Gazzetta*, 1897, 27, ii, 357—367).—The author gives an improved method for preparing nitrohydroxylamine (Abstr., 1897, ii, 24); since this substance behaves as a dibasic acid, it is now called nitrohydroxylamic acid. The sodium or potassium salt is prepared by dissolving caustic alkali in absolute ethylic, or, better, methylic, alcohol, decanting from the aqueous layer, and adding the calculated quantity of hydroxylamine hydrochloride dissolved in alcohol; after filtering and cooling, the requisite amount of ethylic nitrate is added, when the alkali salt soon begins to separate. The *potassium* salt resembles the sodium salt, but is more hygroscopic.

From a discussion of the properties of the new acid, and allied facts, the author assigns to it the constitution $\text{NO} \cdot \text{N}(\text{OH})_2$. It is noteworthy that, on adding nitrobenzene to a sodium ethoxide solution of hydroxylamine hydrochloride, after separating the precipitated sodium chloride, a crystalline deposit slowly separates, which, when dissolved in water and acidified with sulphuric acid, yields the nitrosophenylhydroxylamine, $\text{NO} \cdot \text{NPh} \cdot \text{OH}$, obtained by Bamberger by the action of nitrous acid on phenylhydroxylamine; the author regards it as the oxime of nitrobenzene.

W. J. P.

Phosphorus Oxide. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, 125, 1032—1033).—When a concentrated solution of phosphorous acid is treated in a reflux apparatus with excess of phosphorus trichloride at about 100° , the liquid gradually becomes thick, and eventually a mixture of phosphoric anhydride and phosphorus oxide in equal molecular proportions is obtained. On adding the crude product gradually to water, washing the undissolved portion with cold water, and drying in a dry vacuum, pure phosphorus oxide, P_2O_5 , is obtained as a reddish solid. It can also be prepared by the action of dry air in the dark on a solution of phosphorus in carbon tetrachloride. It is best to have an excess of phosphorus present, and to conduct the operation at a temperature a little above its melting point.

C. H. B.

Salts of Phosphorous Acid. By BRUNO GRÜTZNER (*Arch. Pharm.*, 1897, 235, 693—699).—When a solution of pure phosphorous acid is added to antimony oxide, a *salt* of the composition $\text{SbO} \cdot \text{H}_2\text{PO}_3$ is obtained, crystallising in microscopic needles. No salt could be prepared from the oxide and acid potassium phosphite.

Bismuth oxide gives rise to the salt $\text{Bi}_2(\text{HPO}_3)_3 + 3\text{H}_2\text{O}$; whilst with

aluminium oxide the neutral phosphite is not obtained, but a basic salt, of the probable composition $\text{Al}_2(\text{HPO}_3)_3 \cdot \text{Al}_2(\text{OH})_6$; ferric hydroxide behaves in a similar manner.

The hydroxides of chromium, cobalt, and nickel dissolve readily in phosphorous acid to form very concentrated solutions, but under no conditions could precipitates be obtained. A. W. C.

Amount of Carbonic Anhydride in the Atmosphere. By ARVID G. HÖGBOM (*Chem. Centr.*, 1897, i, 452; from *Svensk. kemisk. Tids.*, 6, 169).—The amount of carbonic anhydride contained in the sedimentary carbonates may be reckoned, according to the author, as equal to about 25,000 times that contained in the air. As only a very small proportion of this quantity can have existed in the atmosphere since there was life on the earth, before this time there must have been a continual supply of this gas from volcanic exhalations. This cannot, however, have been a very constant source, as periods of extreme volcanic activity seem to have been followed by periods of comparative quiescence. Hence, according to the author, the amount of carbonic anhydride in the atmosphere probably varied with the geological periods. E. W. W.

Reduction of Carbonic Anhydride at Ordinary Temperatures. II. The Behaviour of Magnesium. By ADOLF LIEBEN (*Monatsh.*, 1897, 18, 582—588).—This is a continuation of the author's work on the reduction of carbonic anhydride in aqueous solution. (Compare Abstr., 1895, ii, 348.) By the action of platinised magnesium on aqueous solutions of carbonic anhydride, either in the presence of disodium phosphate and ammonium carbonate, or better, of potassium sulphate, to which baryta-water is slowly added, traces only of formic acid are obtained. Under the same conditions, which are those most favourable for the reduction (*loc. cit.*), by using sodium amalgam or aluminium amalgam in place of magnesium, large quantities of formic acid are produced. The author considers that these differences are to be explained by the difference in the thermal energy accompanying the liberation of the hydrogen by sodium amalgam or aluminium amalgam, as compared with that in its liberation by platinised magnesium. W. A. D.

Potassium and Rubidium Fluorosulphates and Fluorophosphates. By RUDOLPH F. WEINLAND and J. ALFA (*Ber.*, 1898, 31, 123—126. Compare Abstr., 1897, ii, 312).—*Tripotassiumdifluorodisulphate*, $\text{K}_3\text{HF}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$, is formed when a solution of potassium sulphate in 40 per cent. hydrofluoric acid is concentrated at a moderate temperature. The salt crystallises in long, colourless prisms with oblique ends, and can be recrystallised from hydrofluoric acid, but not from water; it does not lose weight in a desiccator, but gives off the greater part of its water at 105° , the remainder at 190° . It slowly decomposes in moist air, forming hydrofluoric acid and potassium sulphate, and when heated melts, and then loses water and hydrogen fluoride. A corresponding *rubidium* salt exists, which closely resembles the foregoing in all its properties, but no other analogous compound has been obtained.

Potassium monofluorophosphate, $\text{KHFPO}_3 + \text{H}_2\text{O}$, is formed when the residue obtained by evaporating a mixture of tripotassium phosphate with potassium hydroxide in molecular proportion, is dissolved in hydrofluoric acid and the solution concentrated. It crystallises in colourless, lustrous, quadratic tablets, and decomposes in moist air in a similar manner to the fluorosulphate. It cannot be recrystallised either from water or hydrofluoric acid, and loses hydrogen fluoride when heated. As in the case of the sulphate, the only analogous salt is that of *rubidium*. The authors ascribe the following constitutional formulæ to these salts, $\text{SOF(OK)}_2 \cdot \text{O} \cdot \text{SOF(OK)} \cdot \text{OH} \cdot \text{OH} \cdot \text{POF} \cdot \text{OK}$.

A. H.

Sodium Carbide. By CAMILLE MATIGNON (*Compt. rend.*, 1897, 125, 1033—1035).—Sodium carbide (compare Abstr., 1897, i, 390) is a white solid of sp. gr. = 1.575 at 15°, insoluble in all solvents. Although an endothermic compound, it is not sensitive to either shock or friction. It is not affected by dry air or oxygen at the ordinary temperature, but when gently heated it becomes incandescent, and is converted into sodium carbonate. When thrown into chlorine, it becomes incandescent, with liberation of carbon; bromine attacks it explosively, with formation of carbon bromides; iodine converts it into the carbide, C_2I_4 , melting at 185°. Hydrogen has no action on the carbide; phosphorus combines violently with it at a temperature above 50°, and yields sodium phosphide. When thrown on water, the carbide decomposes violently, with liberation of carbon; but when acted on more gradually it is completely converted into acetylene sodium hydroxide. When placed in hydrogen chloride, the carbide burns, with production of sodium chloride and liberation of hydrogen and carbon, but if suspended in ether, hydrogen chloride converts it completely into acetylene and sodium chloride. In carbonic anhydride or sulphurous anhydride, the carbide becomes incandescent, either at the ordinary temperature or on gently heating, with liberation of carbon. Carbonic oxide has no action on the carbide below 250°; hydrogen sulphide attacks it at above 150°, with formation of acetylene and sodium hydrosulphide. Nitrous oxide and nitric oxide have no action at the ordinary temperature, but the former at 270° and the latter at 150° convert the carbide, with incandescence, into sodium carbonate and carbon. Mixtures of the carbide with oxidising agents are very sensitive to shock and friction. When triturated with several metallic chlorides or iodides, it becomes incandescent, often with explosion. Phosphorus chloride, aluminium chloride, and ferric chloride react with it violently. Mercuric sulphate, yellow mercuric oxide, and lead sulphate are reduced when triturated with it.

Alkylidic iodides and bromides attack the carbide at about 180°, yielding symmetrical acetylenes, $\text{RC}:\text{CR}$, if the iodide or bromide is stable at the temperature of the reaction, but a sodium salt, acetylene, and an olefine if the iodide or bromide is unstable. Monobromobenzene has no action on it at 180°.

Sodium carbide reacts with many organic compounds. Primary and secondary alcohols yield acetylene and a sodium alkyloxide. With aldehydes, ketones, and ethereal salts, there is a violent reaction,

and acetylene is likewise liberated. Anhydrides and acid chlorides decompose the carbide when heated.

Sodium carbide has very much greater chemical activity than calcium carbide, and its reactions with inorganic compounds are almost always violent, carbon being liberated and the sodium behaving as if it were in the free state.

C. H. B.

Ammonium Peroxide. By PETR. G. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 1898, 31, 152—154. Compare this vol., ii, 161).—A better yield of ammonium peroxide is obtained when an ethereal solution of hydrogen peroxide is added at once to an ethereal solution of ammonia. When placed in a freezing mixture of snow and calcium chloride, crystals of the compound $(\text{NH}_4)_2\text{O}_2 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ are deposited. This compound is unstable, and readily deliquesces at the ordinary temperature, first yielding ammonia and hydrogen peroxide, after which a rapid evolution of oxygen begins, and a small amount of ammonium nitrite is formed. Aqueous solutions of the compound also decompose in a somewhat similar manner. Solid ammonium peroxide readily abstracts carbonic anhydride from the atmosphere; it dissolves in alcohol, less readily at -30° than at the ordinary temperature, but is practically insoluble in light petroleum at -30° . It reacts with manganese peroxide in the same manner as hydrogen peroxide does, and dissolves in peruronic acid, yielding the compound $(\text{NH}_4)_2\text{O}_2(\text{UO}_4)_2$.

In one case, crystals of the composition $(\text{NH}_4)_2\text{O}_2 + \text{H}_2\text{O}_2 + \frac{1}{2}\text{H}_2\text{O}$ were obtained.

J. J. S.

Fusion in the Electric Furnace. By GIUSEPPE ODDO (*Real. Accad. Linc.*, 1896, [v], 5, i, 361—364).—The author has investigated the effect of heating lime with varying proportions of silica in the electric furnace, using an alternating current of 40 volts and 120 amperes. On heating granular lime, which readily combines with water, alone, a mass of crystalline scales is obtained; lime in this condition does not slake until after 2—3 days' contact with water.

On heating a mixture of lime and silica in molecular proportion, a crystalline mass of calcium metasilicate, CaSiO_3 , is obtained, which yields gelatinous silica with hydrochloric acid, and does not set when ground and mixed with water, either alone or with lime. A mixture in the proportion of $2\text{CaO} : \text{SiO}_2$ is more refractory in the furnace, but ultimately yields a compact, crystalline mass of calcium orthosilicate, Ca_2SiO_4 , which, when preserved in a desiccator, disintegrates spontaneously to a white, amorphous powder; the salt gives gelatinous silica with hydrochloric acid, and does not set with lime. On heating a mixture in the proportion of $3\text{CaO} : \text{SiO}_2$, a crystalline mass is obtained which spontaneously disintegrates like the orthosilicate, and has approximately the composition $\text{Ca}_2\text{SiO}_4, \text{CaO}$; the disintegrated mass is a mixture of the orthosilicate with lime. The material does not set with lime, and gives gelatinous silica with hydrochloric acid. Similar results are obtained with mixtures of the composition $6\text{CaO} : \text{SiO}_2$.

These experiments indicate that when silica is heated with excess of lime, combination only occurs in the proportions necessary to yield calcium orthosilicate.

W. J. P.

Solubility of Strontium Salts, especially of the Sulphate. By JULIUS WOLFMANN (*Chem. Centr.*, 1897, i, 632; from *Österr. Zeit. Zucker-Ind. u. Landw.*, 25, 986—996).—The author has determined the solubility of freshly precipitated strontium sulphate in water and in solutions of the sulphates, chlorides, and nitrates of the alkalis and alkaline earths, and in solutions of salts of the alkalis with strong organic acids. For temperatures above 100°, a steam boiler which would withstand a pressure of 6 atmospheres was used. At the higher pressures, strontium sulphate probably suffers partial decomposition into sulphide. The various results are tabulated and also represented by curves. E. W. W.

Action of Zinc and Cadmium Hydroxides on Ammonium Sulphate. By JULIUS TROEGER and E. EWERS (*Arch. Pharm.*, 1897, 235, 644—646).—When sodium hydroxide is added to a solution of cadmium sulphate containing small amounts of free sulphuric acid, cadmium hydroxide is formed, whereas ammonium hydroxide causes no precipitation, due to the fact that cadmium ammonium sulphate is formed. It is best prepared by digesting freshly precipitated cadmium hydroxide in ammonium sulphate solution, filtering, and evaporating to crystallisation.

Zinc ammonium sulphate is formed when zinc hydroxide is subjected to similar treatment. A. W. C.

Variations in the Composition of Red Lead. By DURAND WOODMAN (*J. Amer. Chem. Soc.*, 1897, 19, 339—341).—The author finds that the actual amount of red lead in different samples of this substance varies from 41 to 92 per cent. The large amount of lead monoxide sometimes present is easily separable by the lead acetate treatment, and has therefore no part in the chemical constitution of red lead; it appears to be simply an admixture and forms a measure of the incompleteness of the roasting or oxidising process. A. W. C.

Correction [Lead Iodide]. By WILDER D. BANCROFT (*J. Physical Chem.*, 1897, 1, 786).—Lead iodide has been alluded to in the author's paper and that of Talmadge (this vol., ii, 64, 72) as crystallising with 2 molecules of water, but this, as pointed out by Roozeboom, is incorrect, as lead iodide crystallises from water in the anhydrous form. H. C.

Colloidal and Crystalline Copper Hydroxide. By JACOBUS M. VAN BEMMELN (*Chem. Centr.*, 1897, i, 279; from *A. néer.*, 30, 1—24).—By precipitating dilute solutions of copper sulphate with dilute alkalis and washing quickly, according to Spring and Lucion's directions (*Abstr.*, 1893, ii, 210), blue or green precipitates of the hydroxide are obtained from which the whole of the water is only with difficulty expelled. Measurements of the vapour tension attained when the precipitate is kept over sulphuric acid of various concentrations, showed that water is continually given off until the composition of the hydroxide corresponds with the formula $\text{CuO}, \text{H}_2\text{O}$. There is no change in the continuity of the curve obtained by plotting out the results, which would indicate the existence of a hydroxide, $\text{CuO}, 2\text{H}_2\text{O}$, as assumed by Spring and Lucion, although this second molecule of

water is somewhat obstinately retained by the precipitate. The process is not reversible, for although the dehydrated precipitates take up water on exposure to moist air, the same states of hydration are not attained under like conditions of vapour tension as in the former process. The fact that the speed of dehydration cannot be represented by a simple formula, is best explained by assuming that the water is held by the oxide or the hydroxide, $\text{CuO}, \text{H}_2\text{O}$, by adsorption. The adsorbing substance, the hydroxide, $\text{CuO}, \text{H}_2\text{O}$, gradually undergoes a molecular rearrangement, so that its capacity for adsorbing water is altered. Spring and Lucion have proved that such a change occurs even under water. The crystalline hydroxide prepared by Becquerel, Böttger, and others has the composition $\text{CuO}, \text{H}_2\text{O}$, and is stable in presence of salts and at high temperatures. The author has prepared an amorphous hydroxide of the same composition, whose stability and power of retaining water are very similar to those of the crystalline hydroxide.

E. W. W.

Cuprous Sulphate. By J. ALEXANDRE JOANNIS (*Compt. rend.*, 1897, 25, 948—950).—When carbonic oxide is passed into a solution of cupric sulphate containing finely divided copper, or a sheet of platinum coated electrolytically with copper, the gas is slowly absorbed and the liquid becomes colourless. If now the solution is placed in a vacuum, it loses carbonic oxide (free from carbonic anhydride), and when the pressure of this gas in the apparatus falls to 2 or 3 mm., a pellicule of copper separates at the surface of the liquid and the liquid becomes blue. If carbonic oxide is again passed into the liquid, the copper gradually redissolves and the blue colour disappears.

When carbonic oxide is passed into an ammoniacal solution of cupric sulphate containing finely divided copper, the solution becomes colourless, but comparatively little copper dissolves. The whole of the dissolved carbonic oxide cannot be extracted in a vacuum, but part remains in the liquid as ammonium carbonate. There is no separation of metallic copper, and the solution remains colourless. Even in absence of metallic copper, ammoniacal solutions of cupric sulphate are slowly decolorised by carbonic oxide, and then behave in the manner just described. It would seem that, in these cases, cuprous sulphate exists in the solution in combination with ammonia, whilst in the cases first described it exists in combination with carbonic oxide.

C. H. B.

Interaction of Hydrogen Sulphide and Copper Salts. By JOHN B. COPPOCK (*Chem. News*, 1897, 76, 231—232. Compare *Abstr.*, 1896, ii, 562, and Brauner, *ibid.*, 648).—The author has obtained cupric sulphide by adding a solution of copper sulphate acidified with nitric acid to a solution of hydrogen sulphide, but nevertheless admits that, under ordinary circumstances, cupric sulphide is not always obtained by the action of hydrogen sulphide on solutions of copper salts; he, however, does not agree with Brauner's view, that the precipitates consist of mixtures of cuprous and cupric sulphides, but regards them as belonging to the class of compound represented by Linder and Picton (*Trans.*, 1892, 114) by the general formula $n\text{CuS}, \text{H}_2\text{S}$.

D. A. L.

Elementary Nature of the Substance called Cerium. By GRÉGOIRE WYROUBOFF and AUGUSTE V. L. VERNEUIL (*Compt. rend.*, 1897, 125, 950—957).—The authors criticise the results of Schützenberger and of Boudouard (this vol., ii, 164), and consider that the variations observed in the molecular weight of the oxides must be attributed to the presence of impurities. Cerium acetate, for example, is known to be *completely* precipitated by hydrogen peroxide. They also point out that a cerium which Boudouard found to have the atomic weight 91·8, yielded, on further treatment, two fractions with atomic weights of 93·8 and 92·2 respectively, both of which are higher than the original number. C. H. B.

Analysis of an Iron Rail from an Unused Coal Mine. By HENRY P. TALBOT and A. G. WOODMAN (*J. Amer. Chem. Soc.*, 1897, 19, 9—12).—The section of the cast-iron rail examined was taken from the Hub mine at Glace Bay, Cape Breton, where it had lain immersed in water for over twenty years; it had lost its initial density and strength, could be easily cut into fragments, and consisted of an inner core, grey, and very soft, and an outer core, which was black and relatively hard. The following analyses were made.

	Sp. gr.	Loss on ignition.	Total iron.	Total silicon.	Total phosphorus.	Total sulphur.	Graphitic carbon.
Outer shell ...	2·45	7·50	42·00	5·85	3·60	4·65	9·50
Inner shell ...	2·16	8·75	38·10	10·60	3·75	1·41	16·00

Small amounts of manganese and aluminium were also found.

No opinion is offered as to the probable combinations of the constituents, nor as to how the changes in composition have been brought about, but it is interesting to note that articles of steel and wrought iron exposed to the same conditions as this cast-iron rail had apparently suffered no change. A. W. C.

An examination of the action of water of the Hub mine on cast-iron has been recorded by Durkee (*Abstr.*, 1897, ii, 213). A. W. C.

Salts of Ferric Acid. By LUDWIG MOESER (*J. pr. Chem.*, 1897, [ii], 56, 425—437).—An account of these has already appeared elsewhere (*Abstr.*, 1896, ii, 250). C. F. B.

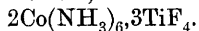
Fluorides, Fluoro- and Fluoroxo-salts of Cobaltammonium Compounds. By ARTURO MIOLATI and G. ROSSI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 183—190 and 223—227).—*Luteocobaltic fluoride*, $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 3\text{HF}$, may be obtained by treating luteocobaltic chloride with silver oxide or carbonate dissolved in dilute hydrofluoric acid and filtering, or by dissolving luteocobaltic chloride in hydrofluoric acid; after concentration, the solution is precipitated by alcohol. It crystallises in small, yellow prisms, is very soluble in water, and although stable at 100°, loses 3HF at 105°. Determinations of its electrical conductivity in aqueous solution at 25° show that the values of μ are nearly the same as those for potassium hydrogen fluoride; being some-

what lower at low values of v and slightly higher at high values of v ; this slight abnormality is doubtless due to hydrolytic dissociation.

Luteocobaltic fluoroborate, $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 3\text{BF}_3 \cdot \text{HF}$, is prepared by adding a solution of luteocobaltic carbonate to a hydrofluoric acid solution of boric acid; it can be recrystallised from water containing hydrofluoric acid, and is stable at $110\text{--}120^\circ$.

Luteocobaltic fluosilicate, $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 2\text{SiF}_4$, is obtained by adding hydrofluosilicic acid to a solution of luteocobaltic carbonate or fluoride.

Luteocobaltic fluorotitanate, $2\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 3\text{TiF}_4 \cdot 2\text{HF}$, prepared by adding a solution of luteocobaltic carbonate or fluoride to a hydrofluoric acid solution of titanic acid, can be crystallised from water containing hydrogen fluoride and loses this gas at 110° . After long preservation in a desiccator over sulphuric acid, it assumes the composition



Luteocobaltic fluoroxymolybdate, $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 2\text{MoO}_2\text{F}_2$, is obtained by adding luteocobaltic fluoride to a hydrofluoric acid solution of molybdic acid; it is crystallised from dilute hydrofluoric acid, and loses weight at 110° . The analyses indicate a tendency to form a compound with hydrogen fluoride.

Luteocobaltic fluoroxytungstate, $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 2\text{WO}_2\text{F}_2$, prepared in like manner, is stable at 110° .

Luteocobaltic fluoroxypuranate is obtained by precipitating a solution of ammonium fluoroxypuranate with luteocobaltic fluoride; it probably has the composition $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot \text{UO}_2\text{F}_2$.

Luteocobaltic fluoroxovanadate, $2\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 5\text{VO}_2\text{F}_2 \cdot 7\text{HF}$, separates on adding luteocobaltic fluoride or carbonate to a hydrofluoric acid solution of ammonium metavanadate and is one of the least stable of this class of salts.

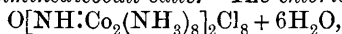
The authors point out that a close analogy exists between the luteocobaltic salts, on the one hand, and the salts of the alkalis, on the other.

W. J. P.

Constitution of Inorganic Compounds. XI. Complex Cobalt-ammonia-compounds. By ALFRED WERNER (*Zeit. anorg. Chem.*, 1898, 16, 109—166)—The insoluble sulphate (fusco-sulphate) obtained by Vortmann (*Monatsh.*, 6, 412) by the oxidation of ammoniacal solutions of cobalt nitrate, is a mixture of two salts, oxodi-imido-octamminedicobalt sulphate and hydrosulphatoimido-octamminedicobalt sulphate.

[With FREDERICK BEDDOW].—Vortmann's fusco-sulphate is most advantageously prepared as follows. Cobalt nitrate (150 grams) dissolved in water (50 grams) is mixed with ammonia (500 grams), the solution gradually heated to boiling and at once filtered; the filtrate is divided into 10 parts, which are placed in flasks and treated with a slow current of air as long as oxycobalt nitrate is precipitated; the dark brown solution is allowed to remain 12 hours, and then filtered and acidified with dilute sulphuric acid. After a few hours, the precipitate of fusco-sulphate and aquopentammine sulphate is separated by filtration and washed with water until all the aquopentammine sulphate is removed. 200 grams of cobalt nitrate yield 7—7.5 grams of fusco-sulphate. The yield, however, varies considerably in each experiment.

Oxodi-imido-octamminedicobalt salts.—The chloride,



is obtained by triturating Vortmann's fusco-sulphate with concentrated hydrochloric acid, whereby it is separated into its two constituents, the above chloride remaining insoluble as a dark green powder; the latter is dissolved in the smallest quantity of water, and the solution filtered into concentrated hydrochloric acid, when the salt crystallises in green, microscopic prisms. It is very easily soluble in water, decomposes and becomes brown when allowed to remain for a short time in neutral solutions, but is more stable in acid solution, and gives characteristic precipitates with potassium ferrocyanide, sodium sulphate, sodium phosphate, potassium dichromate, and platinic chloride. The *bromide*, with $6\text{H}_2\text{O}$, obtained in a similar manner to the chloride, crystallises in microscopic, dark green prisms. The *sulphate*, $\text{O}[\text{NH}:\text{Co}_2(\text{NH}_3)_8]_2(\text{SO}_4)_4 + 6\text{H}_2\text{O}$, obtained by adding dilute sulphuric acid to a solution of the chloride, bromide, or nitrate, is a greenish-grey, microcrystalline precipitate, insoluble in water, but soluble in concentrated sulphuric acid, from which it is precipitated unchanged by dilution with water. The *nitrate*, with $2\text{H}_2\text{O}$, is obtained by treating Vortmann's fusco-sulphate with concentrated nitric acid; on diluting with water, a dark green solution is obtained, and a violet-red, insoluble salt; on mixing the aqueous solution with concentrated nitric acid, the nitrate is precipitated. It crystallises from acidified water in beautiful, dark green prisms, is very soluble in water, and decomposes in neutral solutions with evolution of ammonia and precipitation of cobalt oxide; when heated at 100° , it does not give off its water of crystallisation. The *nitrate*, with $6\text{H}_2\text{O}$, obtained by precipitating a well cooled solution of the preceding salt with a small quantity of nitric acid, crystallises in silky, olive-green needles. When this nitrate is heated with an aqueous solution of ammonium carbonate, a dark brown salt is deposited, which has the composition of a basic tetrammine salt. It is sparingly soluble in cold water, easily so in warm water acidified with acetic acid, and crystallises in black, flat prisms; a salt which is probably identical with this is obtained on treating the nitrate with ammonia. Imido-octammine-dicobalt chloride is obtained from the preceding green nitrate as follows. The green nitrate is warmed with a concentrated aqueous solution of sulphurous acid until it becomes red, the cold mixture is treated with a few drops of nitric acid, and the violet precipitate which is obtained is triturated with concentrated hydrochloric acid; the product is then dissolved in water, the hot filtered solution mixed with concentrated hydrochloric acid, warmed on the water bath for a short time, cooled, and mixed with an equal bulk of 90 per cent. alcohol. After being allowed to remain for 18 hours, the imido-octammine chloride separates as a dark red precipitate.

[With ANTON BASELLI.]—*Hydrosulphatoimido-octamminedicobalt salts*.—The *nitrate*, $[\text{NH}:\text{Co}_2(\text{NH}_3)_8\text{SO}_4\text{H}](\text{NO}_3)_3$, is obtained by treating Vortmann's fusco-sulphate with fuming nitric acid, and, after allowing the mixture to remain for an hour, washing the violet precipitate with water, this operation being repeated three times; the precipitate is then washed with water until the wash water becomes violet-red, and the product recrystallised from dilute nitric acid; it cannot, however, be completely purified by this means. In order to obtain the pure salt, the crude product is converted into the nitrate chloride (described

below), dissolved in the smallest quantity of water, and precipitated with nitric acid; it crystallises in small, violet leaflets, is only sparingly soluble in cold water, and decomposes when heated on the water bath, especially in the absence of free acid. The sulphuric acid contained in this salt cannot be detected by a direct method. The *nitrate chloride*, $[\text{NH}:\text{Co}_2(\text{NH}_3)_8\text{SO}_4\text{H}]\text{Cl}_2\text{NO}_3$, is obtained by dissolving the crude nitrate in hydrochloric acid on the water bath, filtering as quickly as possible, and cooling the filtrate with ice and salt, the crystalline product being washed free from acid with water and with alcohol, and dried on a porous plate over sulphuric acid. It crystallises in slender, microscopic, violet needles, easily soluble in water, and when warmed with hydrochloric acid and water is converted into the imido-octamminedibocalt salt. The aqueous solution gives characteristic precipitates with several metallic salts. The *sulphate*, $[\text{NH}:\text{Co}_2(\text{NH}_3)_8\text{SO}_4\text{H}]\text{SO}_4\cdot\text{SO}_4\text{H}$, is obtained by heating the preceding chloride on the water bath with concentrated sulphuric acid as long as hydrogen chloride is evolved, and then pouring the mixture into ice-cold water; it is a heavy, purple, microcrystalline powder, almost insoluble in water, decomposes when warmed with water, and has an acid reaction towards litmus. The *bromide*, $[\text{NH}:\text{Co}_2(\text{NH}_3)_8\text{SO}_4\text{H}]\text{Br}_3$, obtained by treating the nitrate or sulphate with hydrobromic acid, crystallises in silky, bright-violet needles; the *iodide* is a dark brown crystalline precipitate, obtained on adding sodium or potassium iodide to a solution of the nitrate chloride.

Imido-octamminedibocalt salts.—The *chloride*, $\text{NH}:\text{Co}_2(\text{NH}_3)_8\text{Cl}_4 + 5\text{H}_2\text{O}$, obtained by heating the chloride of the preceding sulphato-series with hydrochloric acid on the water bath and then precipitating with alcohol, crystallises in small, blood-red, lustrous prisms; it dissolves slowly in cold, more readily in warm water, decomposes when heated at 100° , and gives characteristic precipitates with many metallic salts. It is also obtained by rubbing Vortmann's fusco-sulphate with fuming hydrochloric acid and precipitating the clear solution with alcohol. The *nitrate*, with $1\text{H}_2\text{O}$, obtained by treating a solution of the chloride with silver nitrate, crystallises in long, microscopic, red prisms, is less soluble than the chloride, and decomposes in neutral aqueous solutions at 100° . The *sulphate*, with $3\text{H}_2\text{O}$, obtained by precipitating a solution of the chloride with sulphuric acid, crystallises in microscopic, brownish-red leaflets, and is insoluble in water. The *bromide*, with $5\text{H}_2\text{O}$, obtained by treating the sulphate with hydrobromic acid, crystallises in dark, blood-red prisms, and is very similar to the chloride.

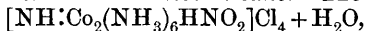
Hydronitrito-imido-octamminedibocalt salts.—The *nitrate*, $[\text{NH}:\text{Co}_2(\text{NH}_3)_8\text{NO}_2\text{H}](\text{NO}_3)_4 + \text{H}_2\text{O}$, is obtained by treating the oxodi-imido-octammine nitrate suspended in water and nitric acid with a concentrated solution of sodium nitrite, and recrystallising the product from dilute nitric acid; it is also obtained by treating the imido-octamminedibocalt nitrate in a similar manner. It crystallises in flat, orange-coloured needles, is precipitated from its aqueous solution by concentrated nitric acid or silver nitrate, and yields characteristic precipitates with many metallic salts. The *chloride*, with $1\text{H}_2\text{O}$, obtained by triturating the nitrate with concen-

trated hydrochloric acid, crystallises in rhombic tablets, is very soluble in water, and is precipitated by hydrochloric acid. The *sulphate*, with $1\text{H}_2\text{O}$, which is quantitatively precipitated by adding dilute sulphuric acid to a solution of the nitrate or chloride, forms small, orange crystals, is insoluble in water, dissolves easily in concentrated sulphuric or hydrochloric acid, and is reprecipitated by dilution with water as sulphate or chloride respectively.

Preparation of the Melanochloride.—Cobalt chloride (50 grams) dissolved in boiling water (30 c.c.) is treated with ammonia (250 c.c. sp. gr. = 0.927), the mixture heated to boiling, and filtered; the filtrate is left in basins for 24 to 36 hours, the red crystalline deposit filtered off, and the filtrate mixed with hydrochloric acid (150 c.c.); a yellowish-brown precipitate is obtained which is separated by filtration, and the dark violet filtrate is allowed to remain in a cool place for 6 hours, when a black, crystalline crust is formed; this is a mixture of salts, consisting of dichloro-aquotriamminecobalt chloride, melanochloride, and the chloride of a new green salt. The last two salts are sparingly soluble, and are obtained as a grey residue when the mixture is treated with water; the bulk of the grey salt is found in the brown precipitate obtained as mentioned above by the addition of hydrochloric acid, and is separated by washing this precipitate with water. When the grey mixture is treated with a hot solution of silver nitrate containing nitric acid, the filtrate, on cooling, deposits dark red crystals of the nitrate of the melano-series. From the mother liquor, a dark green nitrate is obtained which crystallises in large leaflets.

[With FR. STEINITZER.]—*Imidohexamminedicobalt salts* (melano-salts).—The *nitrate*, $\text{NH}[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2]_2 + 4\text{H}_2\text{O}$, prepared as described above, crystallises from water acidified with nitric acid in red, quadratic prisms. It yields a violet sulphate with concentrated sulphuric acid, is not attacked by concentrated nitric acid in the cold, and is completely converted into the corresponding bromide and iodide by hydrobromic or hydriodic acid respectively. The *chloride*, obtained by precipitating an aqueous solution of the nitrate with hydrochloric acid, is a lustrous, greyish-black powder only very sparingly soluble in cold water and has an acid reaction; it dissolves in warm water, and when the solution is heated decomposes, cobalt hydroxide being precipitated. It reacts very easily with silver nitrate, nitrite, and sulphate, yielding the corresponding salts. The *bromide* is a fine, dirty green powder, sparingly soluble in cold water and decomposed by warm water; the *iodide* is a bright brown powder, and is very similar to the bromide.

Hydronitrito-imidohexamminedicobalt salts.—The *chloride*,



is obtained by heating the preceding imidohexamine chloride, dissolved in dilute hydrochloric acid, with sodium nitrite; the filtered solution is then mixed with an equal volume of concentrated hydrochloric acid and boiled, when the salt is deposited in brownish-red leaflets.

E. C. R.

Constitution of Cobalt, Chromium, and Rhodium Bases. By SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1898, **16**, 184—197).—*Basic*

diaquotetramminecobalt sulphate, $\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2 \cdot \text{OH} \cdot \text{SO}_4$, is obtained by dissolving the chloraquotetrammine sulphate in ammonia, and then precipitating with 95 per cent. alcohol, and also in a similar manner from diaquotetrammine cobalt sulphate. It crystallises in small, red tablets, does not give up its water when dried over sulphuric acid, but loses $1\text{H}_2\text{O}$ when heated at 100° , and is converted into the anhydrosalt, which again takes up $1\text{H}_2\text{O}$ when treated with water or when allowed to remain exposed to the air, yielding the hydroxyloaquotetrammine sulphate. Basic diaquotetramminecobalt sulphate dissolves somewhat sparingly in water and yields a faintly alkaline solution, which becomes strongly alkaline after a time, owing to the evolution of one-eighth of its ammonia; it then deposits blackish-brown crystals of the anhydrobasic tetramminediaquodiamminecobalt sulphate. The basic diaquotetrammine sulphate, which is easily soluble in dilute hydrochloric acid, gives the characteristic reactions for diaquotetrammine salts; when warmed with hydrochloric acid, it is completely converted into the chloraquotetrammine chloride. After drying at 100° , it is almost insoluble in water and dilute hydrochloric acid, and when warmed with the latter yields chloraquotetrammine chloride.

Anhydrobasic tetramminediaquodiamminecobalt Salts.—The *chloride*, $\text{OH} \cdot \text{Co}[\text{Cl}(\text{NH}_3)_2(\text{OH}_2)_2] \cdot \text{O} \cdot \text{CoCl} \cdot (\text{NH}_3)_4\text{Cl}$, is obtained by dissolving chloraquotetrammine chloride in dilute ammonia, and after allowing the mixture to remain in a closed flask for 24 hours, precipitating it with 95 per cent. alcohol; it crystallises in small, hexagonal tablets which are deep violet and almost black, it is easily soluble in water, but after a time the solution decomposes, a dark grey, amorphous precipitate being formed. The freshly prepared solution yields characteristic precipitates with many metallic salts. When boiled with water, it does not give off oxygen, and is not therefore an oxycobalt salt. It is decomposed when gently warmed with hydrochloric acid (1:1) and yields chloraquotetrammine chloride, cobalt chloride, chlorine, ammonium chloride, and water; this decomposition is analogous to the decomposition of rhodochromium chloride. When heated with a mixture of hydrochloric acid (2 vols.) and water (1 vol.), it is almost completely converted into the praseochloride. The *sulphate* can be obtained by treating chloraquotetrammine sulphate with ammonia or sodium hydroxide, by treating the chloride with ammonium sulphate or by treating the diaquotetrammine sulphate with ammonia. It crystallises in lustrous, black, rhombic tablets, is very sparingly soluble in water, and when dried in the air contains $5\text{H}_2\text{O}$, which it loses over sulphuric acid; no further loss takes place on heating at 100° , and the dry salt, when treated with water, again takes up $5\text{H}_2\text{O}$ without the slightest alteration in appearance. When warmed with dilute sulphuric acid, it evolves oxygen, and it can oxidise a quantity of oxalic acid corresponding to 1 atom of oxygen for 1 molecule of the salt. The *nitrate* crystallises in microscopic, brown needles; the *dithionate*, *platinochloride*, and *fluosilicate*, are also described.

E. C. R.

Electrolytic Deposition of Nickel. By FRITZ FOERSTER (*Zeit. Elektrochem.*, 1897, 4, 160—165).—Tough, lustrous deposits of nickel of any thickness can be obtained by the electrolysis of aqueous

solutions of the sulphate or chloride at temperatures between 50° and 90°; the deposition is most easily effected from neutral solutions of the sulphate, which may contain from 30 to 100 grams of nickel per litre. The impure nickel anodes are enveloped in parchment paper to retain the insoluble impurities and the electrolyte stirred by air or carbonic anhydride. Lustrous deposits, varying in colour from light grey to tin-white, are obtained with current densities between 0.5 and 2.5 ampères per sq. dcm., but the results are better with the higher current density. With a cathode between two anodes about 4 cm. from it and a current density at the cathode of 1.5 ampère per sq. dcm. the E. M. F. required is 1 volt at 60°. Of the impurities contained in the nickel anodes, carbon, silicon, copper, and manganese are entirely absent from the deposited metal, which, however, contains iron and cobalt in nearly the same proportions as the original, unrefined material. Special experiments showed that iron and cobalt are deposited somewhat more readily than nickel, a result not in accordance with previous determinations which show iron and cobalt in solutions of their sulphates to be slightly more electro-positive than nickel. Iron and cobalt may be quantitatively separated from nickel by the electrolysis of an alkaline solution containing a tartrate, the nickel remaining dissolved. Pure iron is deposited readily in coherent, compact form from a solution of ferrous sulphate containing 10 grams of iron in 100 c.c. at 80°, with a current of 2 ampères per sq. dcm.; the process is, however, soon brought to an end by the formation of basic ferric salts.

A solution of nickel chloride containing 5 to 12 grams of nickel and 0.25 gram of hydrochloric acid in 100 c.c. gives similar results to the sulphate. Temperatures from 50° to 90° and current densities from 0.7 to 3 ampères per sq. dcm. are used, the best results being obtained with the higher temperatures and current densities. Organic materials cannot be used to surround the anode; a piece of linen was used in one experiment, and a dark grey, brittle deposit obtained of about one-half the weight expected and containing 0.6 per cent. of carbon. The solution had a caramel-like smell, owing to organic materials, similar to those observed by Coehn in the electrolysis of strong sulphuric acid with carbon electrodes, having passed into it. It is probable that the commercial electrolytic nickel is obtained by a process similar to those described above.

The deposition of nickel from a solution of the chloride, using carbon anodes, yielded, at first, good results. The yield of metal, however, soon fell off, dark coloured, carbonaceous masses appearing at the cathode, and the solution assuming the caramel-like smell above referred to. The carbon used was the ordinary pressed carbon; possibly better results would be obtained with lead peroxide anodes.

T. E.

Atomic Weight of Nickel. By THEODORE W. RICHARDS and ALLERTON S. CUSHMAN (*Zeit. anorg. Chem.*, 1898, 16, 167—183).—The authors have calculated the atomic weight of nickel from the ratio of silver and silver bromide to nickel bromide. Nickel bromide is prepared by heating finely divided nickel at a red heat in a current of dry bromine vapour, and then subliming the product at a bright red

heat; the sublimed bromide is insoluble in cold water, but dissolves in hot water, and when free from oxide yields a clear solution, which does not give off bromine even when boiled. The sp. gr. = 4.64. The bromide is obtained quite free from oxide by subliming it in a porcelain tube in a current of dry nitrogen and hydrogen bromide, but special precautions have to be taken to exclude oxygen and moisture. The nickel employed in these experiments is purified as follows. The acid solution is subjected to a fractional precipitation with hydrogen sulphide and the nickel sulphide is extracted with dilute hydrochloric acid, washed, dissolved in hot concentrated hydrochloric acid, evaporated to dryness, and the residue dissolved in water; any cobalt which may be present is then separated by fractional precipitation of the solution with sodium hydroxide. The nickel oxide is dissolved in hydrobromic acid, converted into the ammonia compound $\text{NiBr}_2 \cdot 6\text{NH}_3$, and this, after recrystallisation, decomposed by boiling with water, the resulting nickel oxide being reduced to nickel in a current of dry ammonia. The nickel is then converted into bromide by the above method and sublimed. Another sample of nickel obtained by the Mond, Langer and Quincke process was purified by fractional electrolysis.

The analysis of the pure bromide is effected as follows. The sample is dried by heating at 400° in a current of nitrogen and hydrogen bromide, allowed to cool in a current of dry nitrogen, and the nitrogen displaced by dry air. The method of weighing and the apparatus employed are similar to those which the authors employed for weighing magnesium chloride when determining the atomic weight of magnesium. The weighed sample of bromide is dissolved in an Erlenmeyer's flask in warm water, precipitated with the calculated quantity of silver nitrate, and the exact point of precipitation determined in the usual way by means of N/100 solutions of silver nitrate and hydrogen bromide; a slight excess of silver nitrate is then added, and the precipitate of silver bromide separated and weighed.

The first series of seven experiments gave as the atomic weight $\text{Ni} = 58.680$. The second series of seven experiments gave $\text{Ni} = 58.690$. The third series of seven experiments gave $\text{Ni} = 58.691$. ($\text{O} = 16.00$; $\text{Ag} = 107.93$). When $\text{O} = 15.88$, the mean of the results gives $\text{Ni} = 58.25$.
E. C. R.

Chromium Sulphide and Sulphochromites [Thiochromites]. By R. SCHNEIDER (*J. pr. Chem.*, 1897, [ii], 56, 401—424). — *Potassium thiodichromite*, $\text{K}_2\text{Cr}_4\text{S}_7$, is obtained by fusing potassium chromate (1 part) with potassium carbonate (24 parts) and sulphur (24 parts) for 20 minutes at a bright red heat, allowing the mass to cool slowly, and washing it thoroughly but rapidly with cold water. It forms reddish to bluish-grey hexagonal plates with metallic lustre, and has a sp. gr. = 2.77 at 15° . When four times as much chromate is used in proportion to the carbonate and sulphur, or a weight of chromium hydroxide equal to this, a grey powder is left instead of crystals; prolonged washing of this powder with hot water leaves pure chromium sulphide, Cr_2S_3 , as Berzelius stated long ago. Potassium thiodichromite is stable in air; it loses potassium sulphide slowly when it is washed with water; at a red heat in a current of hydrogen, it loses one-seventh of its sulphur,

leaving a steel-blue compound, $K_2Cr_2S_6$, which retains the crystalline form of the thiodichromite; when heated in air, it loses sulphurous anhydride, chromium oxide and potassium sulphide remaining; aqueous potash and ammonia have little action on it; nitric acid and aqua regia decompose it with liberation of sulphur; hydrochloric acid converts it (in the absence of air), without evolution of hydrogen sulphide, into bluish-grey *thiodichromic acid*, $H_2Cr_2S_7$, which retains the form of the original crystals, decomposes into $H_2S + 2Cr_2S_3$ when it is heated in a current of carbonic anhydride, and is very unstable in air, with the oxygen of which it reacts, forming $H_2O + Cr_4S_7$; the last substance loses one-seventh of its sulphur when it is heated in an atmosphere of carbonic anhydride, and leaves very pure chromium sulphide, Cr_2S_3 .

Sodium thiochromite, $Na_2Cr_2S_4$, is obtained by fusing potassium chromate (1 part) with sulphur (30 parts), sodium carbonate (15 parts), and potassium carbonate (15 parts); it forms small, thin crystals, light grey in colour with a shade of brown, and having a metallic to adamantine lustre; its sp. gr. = 2.55 at 15°. In its reactions it resembles the potassium compound described above, except that the very unstable *thiochromic acid*, formed when it is heated with hydrochloric acid in the absence of air, has the composition $H_2Cr_2S_4$, and the compound left when this oxidises in the air, or when sodium thiochromite is treated with hydrochloric acid in the presence of air, has the composition Cr_2S_4 . An extremely convenient method of preparing pure chromium sulphide, Cr_2S_3 , is to treat sodium thiochromite with dilute hydrochloric acid and heat the well-washed product in a current of carbonic anhydride. By shaking sodium thiochromite, suspended in water, with dilute solutions of silver nitrate, lead nitrate, and very faintly ammoniacal copper nitrate, *silver*, *lead*, and *copper thiochromites*, $Ag_2Cr_2S_4$, $PbCr_2S_4$, and $CuCr_2S_4$, were prepared; these are dark brown to black, and retain the form of the original sodium salt in the case of the silver and copper compounds; they are not acted on by water or hydrochloric acid, but nitric acid or aqua regia decomposes them with liberation of sulphur.

C. F. B.

Oxides of Tungsten. By EN. D. DESI (*J. Amer. Chem. Soc.*, 1897, 19, 213—242).—By the action of sulphuric acid on metallic tungsten under varying conditions, oxides of the formulæ WO , W_2O_3 , W_4O_9 , and W_5O_9 have been obtained; they are all blue substances, and the oxide W_2O_3 precipitates silver in brilliant scales from silver nitrate solution, and is decomposed by alkalis into metallic tungsten and a soluble tungstate.

Sulphurous acid acts on tungsten with production of the oxide W_5O_{14} , and reduces tungstic acid, but the lower oxides so formed are exceedingly unstable. The oxide W_3O_8 , obtained by heating ammonium metatungstate to a bright red heat, or by fusing tungstic acid with potassium iodide, is a beautiful, purple substance with a yellow, metallic lustre; it is insoluble in acids and alkalis.

When tungstic acid is heated in an atmosphere of ethylene, a blue substance is formed, which, on heating, becomes rapidly oxidised to yellow tungstic acid, the weight of which is the same as that of the blue substance before ignition.

Tungstic acid is reduced to the metal by fusion with sodium, potassium, or magnesium, or with potassium chloride or bromide; with ammonium chloride, a black oxynitride of variable composition is formed, and with potassium cyanide a black oxynitride, $W_5N_8O_5$. In the last-named experiment, if the temperature is raised very high, metallic tungsten is obtained as bright, silver white globules.

On heating tungstic acid in an atmosphere of cyanogen, an oxynitride, $W_5N_3O_{11}$, is produced.

Tungstic acid is insoluble in concentrated or dilute sulphuric acid hot or cold, whereas molybdenum trioxide is very rapidly dissolved, thus affording a means of separating the two metals. A. W. C.

"The so-called Selective Action" of Potassium Cyanide for Gold. By WILLIAM A. DIXON (*Chem. News*, 1897, 76, 281—282).—The author regards the term "selective action" as inappropriate, and points out that in the treatment of ores with solutions of cyanide, the cyanide dissolves the free metal, which is generally gold, so long as free oxygen or its equivalent is present, and subsequently any remaining cyanide attacks the compounds of the base metals; hence, when comparatively much cyanide and little oxygen is present, as in strong cyanide solutions, much base metal and little gold is dissolved, but in dilute cyanide solutions the conditions are reversed, and so also is the result, so that much gold and but little base metal pass into solution. Referring to the term "cyanicides," the author regards it only as applicable to substances that decompose cyanides, and not to substances that simply render them passive; iron, for instance, as ferric sulphate, destroys cyanides, but in the form of potassium ferrocyanide is stated to dissolve gold in the presence of oxygen in accordance with the reaction $6Au + 2K_4FeCy_6 + 2O_2 + H_2O = 6AuKCy_2 + 2KHO + Fe_2O_3$.

D. A. L.

Preparation of Ammonium and Potassium Platinobromides. By GEORGES MÉKER (*Compt. rend.*, 1897, 125, 1029—1032).—Platinum, even when finely divided, is not attacked by fused ammonium sulphate, nor appreciably by alkali bromides, between 250 and 350°. On the other hand, the metal is rapidly attacked by a mixture of ammonium sulphate with ammonium bromide or potassium bromide, with formation of red ammonium platinobromide, which is readily separated because it is insoluble in ammonium salts. It crystallises from a hot solution in cuboctahedra with the octahedral faces highly developed, but when deposited from a cold solution the cubic faces are by far the more prominent.

With ammonium chloride in place of bromide, the results are indefinite and unsatisfactory; with ammonium or potassium iodide, iodine is liberated. Potassium sulphate and bromide attack platinum in a similar way, but the yield is bad; and this is true also of mixtures of the sulphate and chloride. Ammonium sulphate decomposes potassium platinobromide and converts it into the potassium salt. C. H. B.

Additive Compounds of Potassium Platonitrite. By ARTURO MIOLATI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 355—360).—Potassium platonitrite slowly combines with dry, liquid nitric peroxide, yielding a green, additive compound of the composition $K_2Pt(NO_2)_4 \cdot N_2O_4$; the

presence of a trace of water, and, therefore, of nitrous acid, causes the combination to occur very rapidly. The additive product is stable in a vacuum over calcium chloride, but not over sulphuric acid. At 150° , it yields a red compound, which gives a colourless solution in water, but is again obtained red on evaporation; the red compound is perhaps identical with Vèze's product, obtained from the platonitrite and sulphuric acid. The green substance reacts violently with water, yielding the white hydrate of potassium platonitrite; the reaction with ammoniumhydrate is more violent, and yields platososemidiammine nitrite, $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$.

A green *substance* of the composition $\text{K}_2\text{Pt}(\text{NO}_2)_4 \cdot \text{HCl}$ is obtained by treating potassium platonitrite with cooled concentrated hydrochloric acid; on heating at 150° , it turns red, and on dissolving in a little water and evaporating, potassium monochloroplatonitrite is obtained.

W. J. P.

Mineralogical Chemistry.

Antimony in Bolivian Tin Ores: Volumetric Estimation of Antimony. By FERDINAND GAUTIER (*Actes Soc. Sci. Chili*, 1897, 7, 74—76).—It is argued that the antimony associated with cassiterite in Bolivia must be present as antimonic acid and not as sulphide [this view is, however, quite incorrect (compare this vol., ii, 121)]. Antimony is estimated volumetrically by oxidising with potassium permanganate, and then estimating, with sodium thiosulphate, the iodine which is liberated (in an acid solution) according to the equation $\text{SbCl}_5 + 5\text{KI} = \text{I}_2 + \text{SbI}_3 + 5\text{KCl}$.
L. J. S.

Cohenite in the Telluric Nickel-iron of Niakornak, Greenland. By EMIL W. COHEN (*Meddelelser om Grönland*, 1897, 15, 293—330).—An iron carbide, Fe_2C , has been described, and named chalypite, from the telluric iron of Niakornak, near Jakobshavn in north Greenland, but since cohenite, Fe_3C , has recently been determined in the very similar iron of Ovifak (this vol., ii, 83), it seemed probable that chalypite would probably be identical with cohenite.

This iron carbide was isolated from 50·2847 grams of iron by the action of dilute hydrochloric acid; the nickel-iron dissolved more quickly than meteoric irons; and there was a strong smell of hydrocarbons, but not of hydrogen sulphide. The material thus isolated (52·18 per cent.) consists of greyish-black, crystalline aggregates with good cleavage; analysis gave the results under I, agreeing with $(\text{Fe}, \text{Ni}, \text{Co}) : \text{C} = 3·084 : 1$. The portion soluble in the dilute hydrochloric acid (46·53) gave analysis II, representing approximately the composition of the nickel-iron. The insoluble residue contained carbon (0·06 per cent.) with comparatively much copper sulphide, together with silicate grains, rust, &c. (1·23 per cent.). The bulk analysis of the iron gave III; previous analyses show variations from this. (Anal. I—III by O. Sjöström).

	Fe	Ni	Co	Cu	C	P	S	Residue	Total	Sp. gr.
I.	91.60	1.25	0.37	—	6.44	0.07	—	trace	99.73	7.5124
II.	97.03	2.09	0.71	0.02	—	0.11	0.04	—	100.00	—
III.	93.64	2.00	0.48	0.07	3.72	0.19	1.13	—	101.23	7.2704

Fresh fractures of the iron show a granular structure; on etched surfaces, the resisting cohenite is seen as bright, irregular patches, and Widmanstätten figures were not observed. Iron sulphide was not seen, but its presence is shown by the analyses. The great hardness of the iron is due to the large amount of cohenite present. Embedded in the rust of the iron was a small fragment of ophitic diabase, which is quite different from the Ovifak basalt.

L. J. S.

Calcite with Organic Colouring Matter. By JOHANNES FROMME (*Jahresber. Ver. Naturwiss. Braunschweig*, 1897, 10, 104—113). —The nature of the colouring matter of allochromatic minerals, for example, quartz, calcite, fluorite, &c., is often difficult to determine, and in many cases is not known. The author has examined translucent calcite of a chestnut-brown colour from veins in weathered gabbro in Radauthal, near Harzburg, in the Harz. The material is crystalline, and partly in well-developed, acute rhombohedra (—4R). Iron and manganese are absent. When heated in a closed tube, the mineral emits a penetrating odour and gives off some water; when ignited, it yields a pure white lime, and from the weight of this is calculated 99.15 per cent. of CaCO_3 , leaving 0.85 per cent. for other volatile constituents. That organic matter is present is also shown by the reduction of potassium permanganate. The colouring matter is not extracted from the powdered mineral by water, ammonia, alcohol, ether, benzene, &c. The calcite is completely dissolved in hydrochloric acid, with emission of an asphalt-like smell, frothing, and separation of brown flocks; the filtrate is clear and of a wine-yellow colour.

The brown, flocculent material agrees in all its characters with Berzelius' apocrenic acid. When dry, it is blackish-brown and earthy; it has an astringent taste, and is slightly acid to litmus. It is only slightly soluble in water, giving a yellow solution, but it is easily soluble in alcohol and alkalis. From the ammonia solution, lime water precipitates the calcium salt as dark brown flocks. Nitrogen is absent, and in this it differs from humic and other acids. By dissolving a large quantity of calcite, 0.2310 per cent. of apocrenic acid was obtained. The colouring matter in the yellow hydrochloric acid solution of the calcite was separated by dialysis, and on evaporating, another acid was obtained in the form of brownish-black flocks; this is only sparingly soluble in water and alcohol, but readily in hydrochloric acid and alkalis. It is present in the calcite to the extent of 0.0135 per cent.

Since these substances cannot be extracted from the calcite by reagents, they must exist in combination. From a solution of calcium hydrogen carbonate containing an ammonia solution of apocrenic acid, artificial crystals of calcite were obtained; these are acute rhombohedra of a brownish-yellow colour, exactly like the natural mineral.

L. J. S.

[**Dolomite from the Transvaal.**] By FREDERICK H. HATCH (*Quart. Journ. Geol. Soc.*, 1898, **54**, 73—99).—In a paper on the geology of the Witwatersrand and other districts in the Southern Transvaal, the following analysis, by G. T. Prior, is given of crystalline dolomite.

CaO.	MgO.	FeO.	MnO.	SiO ₂ .	CO ₂ +H ₂ O.	Total.	Sp. gr.
29·61	19·71	1·35	1·18	0·94	46·69	99·48	2·88.

This corresponds with CaCO₃, 52·87 ; MgCO₃, 41·39 , FeCO₃, 2·17 ; MnCO₃, 1·99 per cent. Another specimen was found to contain 2·81 per cent. of silica, and every variation appears to exist between dolomite and chert. In the weathered rock, the siliceous ribs stand in relief, giving the surface a wrinkled appearance, hence the name "elephant rock" ; the weathered surfaces are brown, owing to the separation of the manganese as wad.

L. J. S.

[**Datolite from Radauthal.** By JOHANNES FROMME (*Jahresber. Ver. Naturwiss. Braunschweig*, 1897, **10**, 170—174).—Veins of datolite occur in the gabbro of Radauthal, near Harzburg, in the Harz ; it is massive with a granular structure, and is white, often with a greenish tinge. The mean of two analyses by Schwikkard is

SiO ₂ .	B ₂ O ₃ .	Al ₂ O ₃ and traces of Fe.	CaO.	H ₂ O.	Total.	Sp. gr.
37·65	[20·36]	1·18	34·91	5·90	100·00	2·951

When the aluminium is taken as replacing boron, this agrees closely with the usual formula, HCaBSiO₅ ; the existence of the isomorphous molecule, HCaAlSiO₅, corresponding with euclase, HBeAlSiO₅, is therefore assumed. Full details of the method of analysis are given.

L. J. S.

[**Quartz-barytes Rock from Salem, Madras.** By THOMAS H. HOLLAND (*Records Geol. Survey India*, 1897, **30**, 236—242).—This rock forms a network of veins, from mere strings to several feet across, in the pyroxenic and other gneisses near Alangayam in the Tirupatur taluk, Salem district, Madras Presidency. The average sp. gr. of the rock is 3·005, from which is calculated 69·2 per cent. of quartz, and 30·8 of barytes ; small amounts of galena, pyrites, ilmenite, hæmatite, and limonite are also present. The quartz is white to grey, and forms an aggregate of interlocking crystals. The grey to pink barytes individuals are 2—3 inches across, and are sometimes bounded by crystal faces ; analysis of crystals gave

BaSO ₄ .	CaSO ₄ .	FeO ₃ .Al ₂ O ₃ .	SiO ₂ .	Loss on ignition.	Moisture.	Total.	Sp. gr.
94·15	4·01	0·93	0·63	0·26	0·04	100·02	4·30

The low sp. gr. is due to the partial replacement of barium by calcium. This rock, which has the appearance of a pegmatite, is presumably of igneous origin ; from the magma, the barytes has crystallised, as a rule, before the quartz. Such a mode of occurrence of barytes is unique.

L. J. S.

[**Hornblende from Ivrea, Piedmont.**] By FRANK R. VAN HORN (*Tsch. Min. Mitth.*, 1897, **17**, 409—414).—In a petrographical paper

(pp. 391—420) on the norite and related rocks from the neighbourhood of Ivrea in Piedmont, the following analysis (I) of hornblende is given. This was isolated from a hornblende-gabbro, from Pavone, containing plagioclase (near bytownite), 33; hornblende, 27; diallage, 20; hypersthene, 5; magnetite, 10, and green spinel, 5 per cent.; the bulk analysis of the rock is given under II, also trace of P_2O_5 ; sp. gr. = 3.18. The brown hornblende has a cleavage angle of $124^\circ 18'$, and an extinction angle on $b(010)$ of 15° ; sp. gr. = 3.22. The results of the analysis (I) agree approximately with the orthosilicate formula, $R'_2R''_4R'''_2Si_4O_{16}$; the mineral, therefore, resembles the syntagmatite of Vesuvius and Jan Mayen.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	39.58	trace	14.91	4.01	10.67	trace	13.06	11.76	2.87	0.62	2.79	100.27
II.	39.84	0.08	19.71	7.73	8.89	trace	7.33	13.52	1.59	0.53	0.86	100.08

L. J. S.

Phosphatic Chert. By J. H. KASTLE, JOS. C. W. FRAZER, and GEO. SULLIVAN (*Amer. Chem. J.*, 1898, 20, 153—159).—The authors give analyses of thirty-nine samples of chert of the Lower Hudson formation, which are remarkable for the large percentage of phosphoric acid they contain. The average of the analyses is 1.684 per cent. P_2O_5 , their range being from 0.179 to 3.5 per cent. P_2O_5 . It thus appears that the chert contains from four to five times as much phosphoric acid as either the soil or limestone rock in the same locality.

W. A. D.

Talcose-schist from Canton Valais. By THOMAS G. BONNEY (*Geol. Mag.*, 1897, N.S., [iv], 4, 110—116).—In the schists near Zinal in the Val d'Anniviers, Switzerland, is a soft "ovenstone" which is used for constructing stoves. The dominant tint of this stone is lead-grey, inclining to a dull lavender, and the structure is fissile, with greenish-white seams. From a microscopical examination, the minerals present seem to be talc and chlorite, with grains of magnetite and pyrites. Analysis of the rock by Miss E. Aston shows that it might consist of talc, tremolite, and a chlorite, in approximately equal amounts.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	NiO.	CO ₂ .	H ₂ O.	Moisture.	Total.
44.94	5.47	1.75	3.47	8.76	25.57	2.90	1.22	5.40	0.35	99.83

Also traces of Cr_2O_3 , MnO, and CuO; sp. gr. = 2.90. Other specimens contained 0.5 and 0.25 per cent. of NiO; the water and carbonic anhydride also vary. The nickel seems to be present in this rock, as well as in various Alpine serpentines, as a silicate, possibly noumeite, and not as awaruite (*Abstr.*, 1896, ii, 611).

The examination of this rock confirms the view that a talcose-schist may be only a further stage in the alteration of a much crushed serpentine, or the third remove, at least, from a peridotite.

L. J. S.

Rocks [and Felspar] from the Volcano Osorne, Chili. By WILLY BRUHNS (*Ber. naturforsch. Ges. Freiburg i. B.*, 1897, 10, 201—214).—A description is given of a collection of rocks, comprising

mainly felspar-basalts poor in olivine, from the volcano of Osorne, in south Chili. Porphyritic crystals of felspar from one of these rocks gave analysis I, corresponding with a bytownite, Ab_1An_4 . The angle of optical extinction on the basal plane is 20° ; sp. gr. = 2.731. The crystals are often rich in zonally arranged enclosures, but for the analysis all impure material could be separated by the electromagnet. The bulk analysis of the rock is given under II; felspar, augite, magnetite, and brown glass are present.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.
I.	48.52	32.01	0.63	—	16.41	trace	—	2.76	100.33
II.	54.58	23.21	5.33	2.44	11.37	0.76	—	2.69	100.38

L. J. S.

Olivinite and Picrotitanite from Magnolia District. By MILTON C. WHITAKER (*Proc. Colorado Sci. Soc.*, 1898, Feb. 5, 14 pp.).—The granite of the Magnolia district in Boulder Co., Colorado, is intersected by a dyke of igneous rock; the dark grey to purplish rock of this dyke contains serpentinous nodules, enclosing some olivine, magnetite, picroilmenite, garnet, calcite, chlorite, biotite, muscovite, and a zeolite. Analysis of material freed from garnet and picroilmenite gave the results under I; sp. gr. = 2.73. It is probably an altered olivine rock.

	SiO ₂ .	TiO ₂ .	P ₂ O ₅ .	CO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	22.07	0.34	0.60	8.77	11.86	4.67	3.35	10.48	25.39	3.64	3.29	5.61	100.07
II.	0.53	51.92	—	—	—	12.82	23.70	—	12.05	—	—	0.49	101.51

The picroilmenite occurs in this rock as black, lustrous grains and nodules; sp. gr. = 4.44. The mean of two analyses by different methods is given under II; the ferrous oxide is possibly too low. This gives MgO, FeO, 2TiO₂, that is, an ilmenite rich in magnesia (compare this vol., ii, 122).

L. J. S.

Chemical Evidence for the Existence of Organisms in the Oldest Rocks. By CHARLES CALLAWAY (*Proc. Liverpool Geol. Soc.*, 1897, 8, 98—103).—Since limestones, graphite, apatite, iron ores, and even metallic sulphides may in some cases have been formed by organic agencies, it has sometimes been assumed that the presence of these in association with gneiss is evidence of the existence of organic remains in the oldest rocks. It is here pointed out that this reasoning is not sound, since these minerals can also be of igneous or of metamorphic origin.

L. J. S.

Spectrographic Analysis of Meteorites. By W. NOEL HARTLEY and HUGH RAMAGE (*Sci. Proc. Roy. Dublin Soc.*, 1898, N.S. 8, 703—710).—The authors, who have previously made spectroscopic examinations of iron ores (*Trans.*, 1897, 533), have now extended their observations to meteorites; irons, siderolites, and stones of 13 falls being examined. Lines of the following elements are identified, and measurements between wave-lengths 6000 and 3200 are given: calcium, iron, nickel, cobalt, chromium, gallium, lead, manganese, silver, copper, sodium, potassium, rubidium, and magnesium. The proportions of these vary to some extent in the different meteorites.

Copper, lead, and silver are common constituents, as is also the case in iron ores and manufactured irons. Gallium is present in all the irons but not in all the stones examined. Chromium and traces of manganese are present in the stones, but as a rule not in the irons. Meteoric iron differs from telluric iron in containing nickel and cobalt in considerable amount, whilst manganese is only present in traces.

The olivine from an Atacama siderolite was found to contain sodium, potassium, magnesium, calcium, iron, nickel, chromium, copper, silver, lead, and traces of strontium and manganese. L. J. S.

Water of the "Marzis" Spring near Geneva. By C. RUST (*Arch. Sci. phys. nat.*, 1898, [iv], 5, 162—165).—Clear, colourless water from the "Marzis" spring, at Plongeon, near Geneva, gave the following results on analysis: K_2O , 0.00583; Na_2O , 0.00879; HN_3 , traces; MgO , 0.02638; CaO , 0.18310; $Al_2O_3 + Fe_2O_3$, 0.00103; MnO , traces; SO_3 , 0.03376; P_2O_5 , 0.00019; N_2O_5 , traces; Cl , 0.00939; total CO_2 , 0.33685; SiO_2 , 0.01308; N , 0.01327; O , 0.00658; total, 0.63825, in grams per 1000 c.c.; sp. gr., 1.000223; temperature, 9.15° . This forms a good table water, and closely resembles the medical water of the Cachat spring at Evian. L. J. S.

Comparative Examination of the Montecatini Chlorinated Waters. By LUIGI LUCIANI, UBERTO DUTTO, and D. LO MONACO (*Rend. Accad. Lincei*, 1896, [v], 5, ii, 81—93. See this vol., ii, 244).

Physiological Chemistry.

Peptic Digestion. By WILHELM CRONER (*Virchow's Archiv.*, 1897, 150, 260—271).—A number of experiments are recorded, the object of which is to discover the relationship between the amount of pepsin and hydrochloric acid which will produce the most efficient digestion of albumin. The amount of pepsin should be over 0.1 per cent., and of hydrochloric acid between 0.05 and 0.1 per cent. W. D. H.

Influence of Alcohol on Digestion. By RUSSELL H. CHITTENDEN, LAFAYETTE B. MENDEL, and HOLMES C. JACKSON (*Amer. J. Physiol.*, 1898, 1, 164—209).—On the introduction of alcohol or alcoholic beverages into the mouth in dogs and men, the flow of saliva is transiently increased; and on its introduction into the stomach, the gastric secretion is increased in quantity, acidity, and proteolytic activity. Alcoholic drinks retard the activity of digestive fluids, but in the living animal this is counterbalanced by the increased secretion of the juices mentioned, as well as by the rapid absorption of the alcohol given; experiments with test meals, with and without alcohol, gave practically the same results. There is little or no direct influence on pancreatic or intestinal juices. W. D. H.

Inversion of Cane-sugar in the Stomach. By S. J. FERRIS and GRAHAM LUSK (*Amer. J. Physiol.*, 1898, 1, 277—281).—The inversion of cane sugar that occurs in the stomach is very considerable, and is due to the hydrochloric acid present. Thus, in the stomach of a living rabbit, 90 per cent. was inverted in six hours and a half; this is even greater than the inversion that occurred in a beaker, using 0.2 to 0.3 per cent. hydrochloric acid, and is probably due to the continual movement of the gastric contents. W. D. H.

Influence of Borax and Boric Acid on Nutrition. By RUSSELL H. CHITTENDEN and WILLIAM J. GIES (*Amer. J. Physiol.*, 1898, 1, 1—39).—Doses of borax up to 5 grams, even when continued for some time, have no effect on the nutritional changes of the body. Larger doses (5 to 10 grams daily) increase proteid metabolism, and larger amounts of nitrogen, sulphuric acid, and phosphoric acid are excreted in the urine.

Boric acid up to 3 grams daily has no effect. In larger doses, borax retards the assimilation of proteid and fatty food, whilst with very large doses there is a diarrhœic tendency.

Borax decreases the volume of the urine, and, passing as such into this excretion, raises its specific gravity and renders it alkaline. Both borax and boric acid are rapidly eliminated, and so no cumulative action can result from their daily use. They have no influence on putrefaction in the intestine. W. D. H.

Metabolism during Inanition. By JOHAN E. JOHANSSON, E. LANDERGREN, KLAS SONDÉN, and ROBERT A. A. TIGERSTEDT (*Chem. Centr.*, 1897, i, 180—181; from *Skand. Arch. f. Physiol.*, 7, 29).—The experiments made on a man lasted nine days, five of which were hunger-days. The intake and output, including those in the lungs, were estimated. The average loss of weight per diem during hunger was 1.48 per cent. (Cetti, 1.54, Succi, 0.83). W. D. H.

Metabolism in Fatty Degeneration. By GRAHAM LUSK (*Proc. Amer. Physiol. Soc.*, 1898, 5—6; *Amer. J. Physiol.*, 1).—The proteid molecule may yield 60 per cent. of dextrose in metabolism. Hence the large yield of sugar produced by phloridzin in starving animals. Experiments on dogs in which acute fatty degeneration had been produced by phosphorus poisoning, show that no sugar is present, and on giving phloridzin no excess of sugar is eliminated; either, then, the sugar is burnt as soon as it is formed, or it is converted into another substance. The former alternative is improbable on account of the high proteid metabolism, for its oxidation would reduce proteid metabolism; it is therefore probable that the sugar is converted into another substance, namely, the fat which appears within the cells of the body. W. D. H.

The Rôle of Sugar in Animal Metabolism. By NATHAN ZUNTZ (*Chem. Centr.*, 1897, i, 248; from *Du Bois Reymond's Archiv.*, 1896, 538).—The paper combats the view advanced by Seegen and Chauveau, that sugar is the chief source of muscular energy. Fat, and a portion of the proteid, acts similarly. There is no evidence that the fat is transformed into carbohydrate before it is capable of utilisation in this way. W. D. H.

Muscular Work and Glycogen. By JOSEF SEEGEN (*Chem. Centr.*, 1897, i, 247; from *Du Bois Reymond's Archiv.*, 1896, 383, 407; 511—523).—A further contribution to a much debated subject. Experiments on dogs show that with muscular work the muscular glycogen diminishes, but only sufficiently so to account for from 3 to 11 per cent. of the work done. Sugar is regarded as the main source of energy, and this view is not regarded as antagonistic to Pflüger's.

W. D. H.

The Sugar-yielding Substances of the Body. By FERDINAND BLUMENTHAL (*Chem. Centr.*, 1897, i, 938; from *Berlin. klin. Woch.*, 34, 245—248).—The artificial production of sugar from albumin is stated to be probable, but not proved. Various nucleo-proteids, however, yield pentose.

W. D. H.

Hepatic Glycogenesis. By FREDERICK W. PAVY (*J. Physiol.*, 1898, 22, 391—400).—A further contribution to the discussion which has arisen between the author and D. Noël Paton. The evidence, both *a priori* and experimental, is regarded as being in favour of the ferment theory of the *post-mortem* change of glycogen into sugar, and against that advanced by Paton that the change is a 'vital' one due to an exaggeration of the katabolic side of metabolism.

W. D. H.

Papain-proteolysis. By RUSSELL H. CHITTENDEN, LAFAYETTE B. MENDEL, and H. E. McDERMOTT (*Amer. J. Physiol.*, 1898, 1, 255—276).—Certain recent writers have stated that papain digestion does not yield true peptone, but the present experiments show that, although different preparations of papain vary in activity, the majority are energetic, and produce, as Martin showed, large quantities of proteose, especially deuteroproteose, and relatively a very large amount of true peptone. When injected into the circulation, these substances produce the usual physiological effects on blood-pressure, coagulability of the blood, and urinary secretion. When the deuteroproteose is injected, it appears if the kidneys are active, in the urine partly as such, partly as true peptone. This confirms a previous observation of Neumeister's.

W. D. H.

Absorption of Iron in the Intestine in its Relation to Blood-formation. By M. CLOETTA (*Chem. Centr.*, 1897, i, 393—394; from *Arch. exp. Path. Pharm.*, 38, 161—174).—The absorption of the iron in *ferratin natr. sol.*, in loops of a dog's small intestine amounts to from 19 to 23 per cent. The amount of iron in the liver is greater when organic compounds of iron are given; it is considered probable that inorganic compounds must be first converted into iron albuminate before absorption is possible. No increase in the hæmoglobin of the blood was found.

W. D. H.

Origin and Properties of Lymph. By LEON ASHER and A. G. BARBERA (*Zeit. Biol.*, 1898, 36, 154—239).—The blood-vessels normally absorb a part of the tissue-juice. The lymph carries toxic products of metabolism, which, however, are capable of change, and thus of future use to the organism; lymph is not qualitatively the same as blood plasma, but is largely a product of the work of the organs, and when

injected into the blood stream it produces certain characteristic effects. In the salivary glands, when secretion occurs, there is not only a change in the blood-vessels, but the flow of lymph is increased. Increased work of the thyroid increases the lymph flow from that organ. On pure proteid diet, the flow of lymph in the thoracic duct is increased; the increase here was parallel with the increase of nitrogen in the urine, that is, with the work of absorption.

Intravenous injection of crystalloid substances (like sugar) is only followed by increase of the lymph stream if there is simultaneously an increase in glandular activity. Intravenous injection of peptone causes an increase of the lymph formation by the liver, as Starling showed; but there is at the same time an enormous (eight-fold) increase in the flow of bile. The secretion hypothesis of lymph formation thus receives strong confirmation. The increase of the lymph stream which occurs when the vena cava inferior is blocked is probably also due to increase in the work of the liver.

A distinction must be drawn between "nutrition fluid" and lymph. The fluids of the serous cavities, synovia, endolymph, perilymph and aqueous humor cannot be functionally reckoned as lymph. The "nutrition fluid" is a transudation from the blood, and the tissue cells play a part in regulating the transudation. By the work of the cells of the organs, katabolic products arise which alter the osmotic relationships of lymph and blood. The changes which the blood stream undergoes during the physiological work of the organs also take a share in determining the condition of the lymph stream.

The lymphatic glands have the power of altering the katabolic products brought to them by the lymph; these products form the normal stimulus to these glands, and one result is the formation of leucocytes. The leucocytes undertake the change in the katabolic products, so that, finally, the lymph once more resembles blood-plasma; in other words, the lymph leaving the lymphatic glands on its way to the blood stream has certain differences from that contained in the different lymphatic channels to these glands.

W. D. H.

Similarity of Structural Changes Produced by Want of Oxygen and by Certain Poisons. By SIDNEY P. BUDGETT (*Amer. J. Physiol.*, 1898, 1, 210—214).—The visible changes of structure shown by certain protozoa (*amœba*, *paramœcium*, &c.) when deprived of oxygen are described and figured; these may be exactly reproduced by the action of certain poisons, such as potassium cyanide. This indicates either that these poisons prevent oxidation or that lack of oxygen produces toxic substances. Potassium cyanide reduces the resistance shown by *paramœcium* to the entrance of water, and leads to the taking up of water probably by hastening molecular breakdown, and so increasing the osmotic pressure within the cell.

W. D. H.

Reduction of Arsenic Acid by Juices of Organs. By B. BINZ (*Chem. Centr.*, 1897, i, 394; from *Arch. exp. Path. Pharm.*, 38, 259—265).—Arsenious acid in a weak alkaline solution is oxidised to arsenic acid by the fresh juice of the small intestine, of the spleen, and especially of the liver. The present research is directed to determine

whether any of the fluids of the body produce the opposite effect. The blood (of ox and calf) do so feebly, rabbit's liver strongly. After feeding on arsenic acid, small quantities of arsenious acid are found in the urine. Fresh rabbit's urine carries out the reduction very feebly, muscular tissue not at all, and the living small intestine feebly.

W. D. H.

Salivary Secretion. By D. F. F. GRÜNBAUM (*J. Physiol.*, 1898, 22, 385—390).—Heidenhain stated that the percentage of salts in saliva varies directly as the rate of secretion; his own figures show, however, some discrepancies. In the present research, the submaxillary gland was made to secrete against resistance; under these circumstances, less saliva is secreted and the percentage of salts in it increases. Hence there is decrease in the amount of work done, which is greater than the increase of work in consequence of external resistance, and a rise in the organic substances of the secretion.

W. D. H.

Composition of Human Saliva. By RUSSELL H. CHITTENDEN (*Proc. Amer. Physiol. Soc.*, 1898, 3—5; *Amer. J. Physiol.*, 1).—Human saliva, although ordinarily alkaline to litmus or lacmoid, is acid to phenolphthalein. The alkalinity is therefore due to alkali phosphates, acid phosphates being also present. The average numbers show an alkalinity equal to 0.14 per cent. of sodium carbonate, and an acidity such that 1 gram of saliva requires 0.06 milligram of sodium hydroxide to neutralise it. Alkalinity, acidity, and amylolytic power are greater in saliva coming from glands after a long rest, that is, collected before breakfast, than in that secreted an hour after the meal. The increased amylolytic activity is not due to the salts, but to an increase in the organic substances (including the enzyme). Alcoholic drinks increase the amylolytic activity of saliva.

W. D. H.

Urine of *Echidna aculeata*. By RICHARD NEUMEISTER (*Zeit. Biol.*, 1898, 36, 77—81).—The urine from the *Echidna* was collected from the cloaca without contamination with fæces. The animal is wholly carnivorous, and, contrary to expectation, its urine was found to be neutral in reaction. This animal has therefore the power, which is absent in the higher mammals, of being able to completely neutralise by ammonia the acid substances which originate from proteids. The urine contains no uric acid, and no alloxuric bases. Urea accounts for 81.14 and ammonia for 6.98 per cent. of the nitrogen in the urine; the remainder of the nitrogen is in some substance or substances not yet identified.

The urine of the bull frog and of the crocodile, which were likewise kept on flesh diet, is also neutral or faintly alkaline. The same is true for the tortoise (Müller and Magnus), but no details as to food are given. In a starving tortoise (Marchand), the urine was faintly acid. Nebelthau found the urine of the edible frog fed on worms to be faintly acid or neutral.

W. D. H.

Physiological Action of Normal Dinitriles. By JEAN F. HEYMANS and PAUL MASOIN (*Chem. Centr.*, 1897, i, 1240—1241; from *Arch. Pharmacodynamie*, 3, Heft 1 and 2).—The fatal doses of cyanogen, and of the dinitriles of malonic acid, of succinic acid, and of

pyrotartaric acid are given in respect to frogs, rabbits, dogs, and pigeons. Speaking generally, the dose rises with the molecular weight. Sodium thiosulphate is stated to be antagonistic to the dinitriles.

W. D. H.

Physiological Action of Choline, Neurine, and allied Substances. By FREDERICK W. MOTT and WILLIAM D. HALLIBURTON (*Proc. Physiol. Soc.*, 1898, 34—35. Compare Abstr., 1897, ii, 222).—In a previous communication, it was shown that cerebro-spinal fluid removed from cases of brain atrophy (particularly from cases of general paralysis of the insane) produces a fall of blood-pressure. The material in the fluid that produces this effect is not proteid, nor is it of inorganic nature, but is precipitable by phosphotungstic acid, and is therefore probably alkaloidal. Dilute solutions of choline hydrochloride produce the same effect on blood-pressure. The related alkaloid neurine produces a different effect, a preliminary fall of pressure being usually followed by a marked rise.

The present research shows that the substance in the cerebro-spinal fluid which produces the effect is choline, characteristic crystals of the platinochloride having been prepared from the fluid.

The fall of blood-pressure which occurs is only partly of cardiac origin. There is slowing of the heart, but this is often not very marked, and as tracings with Barnard's cardiometer showed, is accompanied with an increased output.

The main cause of the fall is vascular dilatation. This was investigated by the use of air-plethysmographs. In the case of the limbs, there is no evidence of active dilatation; the volume of the limb is, in fact, slightly diminished; this appears to be secondary to the general fall of arterial pressure. The same is true for the kidney; the lever of the kidney oncometer falls with the blood-pressure. In the case of the intestines, however, there is marked vascular dilatation. (For a description of the intestine oncometer used, see Edmunds, *J. Physiol.*, 1898, 22, 380.)

Although the principal interest in this work centres round the fact that the toxic material in the specimens of cerebro-spinal fluid in question is choline, a good many experiments have been made on neurine as well. The primary fall in the arterial pressure is of cardiac origin; the slowing of the heart and deepening of the respiration are very marked symptoms; usually, this is followed by a rise of pressure, due to constriction of peripheral vessels. In some cases, this latter phase is absent, and the heart remains permanently slowed and the animal may die, whilst in some few cases, using small doses (1 or 2 c.c. of a 0.1 per cent. solution of the hydrochloride), there is only the second phase, a rise of pressure with peripheral constriction of the intestinal and kidney blood-vessels.

W. D. H.

Physiological Action of Derivatives of Cocaine. By GAETANO VINCI (*Chem. Centr.*, 1897, i, 1217; from *Du Bois Reymond's A. chiv.*, 1897, 163—170).—It has previously been shown that eucaine acts in a manner similar to cocaine (this vol., ii, 86). The same is true for methylic 4-benzoxy-1:2:2:6-tetramethylpiperidine-4-carboxylate formed from eucaine by the substitution of a methyl group for hydrogen.

The action of trans-benzoylmethylvinylidiacetone-alkamine (4-benz-oxy-1 : 2 : 2 : 4-tetramethylpiperidine) was also investigated. Although this is a local anæsthetic, it causes stimulation and hyperæmia at the place of application, produces a curare-like action on motor nerve-endings, and in large doses paralyses the vagus nerve-endings in the heart.

W. D. H.

Physiological and Therapeutic Effects of Spermine. By ALEXANDRE PEHL (*Compt. rend.*, 1897, 125, 959—961).—Spermine, $C_5H_{14}N_2$, occurs in almost all the organs of the body, and even when present in small quantities accelerates the oxidation of organic and inorganic substances in the same manner as a ferment (*Compt. rend.*, 1892 and 1893). Many observers have found that when administered by ingestion or subcutaneous injection, it has beneficial effects in a very wide range of maladies. These effects the author attributes to its power of restoring or increasing intra-organic oxidations, facilitating the elimination of waste products and destroying antitoxins or toxins of microbic origin. He finds that, when it is administered, the ratio of nitrogen in the urea to the total nitrogen is restored to normal, or in other words, the injurious intermediate nitrogenous compounds are reduced in quantity. Direct experiment shows that the leucomaines and nitrogenous extractive substances in the urine diminish. The ratio of urea to chlorides also diminishes, notwithstanding the increase in the total quantity of urea; the ratio of uric acid to phosphoric acid is slowly restored to normal; the ratio of total phosphoric acid to neutral phosphates is distinctly reduced, and the consequent increase in the alkalinity of the blood is favourable to oxidation. On the other hand, spermine seems to have no influence on the intestinal fermentations, and the ratio of total sulphuric acid to sulphonic acids is not altered; it is therefore without effect on intestinal auto-intoxication.

C. H. B.

Chemical and Physiological Studies on Phloridzin and Allied Compounds. By MAX CREMER (*Zeit. Biol.*, 1898, 36, 115—127).—In animals in which phloridzin-diabetes has been produced, the urine, after removal of the sugar by fermentation, is lævorotatory. Moreover, phloridzin can be separated as such from the urine; its lævorotatory action was, therefore, attributed to phloridzin; but, if this is the case, the quantity of phloridzin in the urine as estimated by the polarimeter is greater than the quantity administered. Phloridzin is, therefore, not the only lævorotatory substance in the urine, but some of that which is given must be changed into another, more strongly lævorotatory substance. The present research considers some of the properties of phloridzin itself (solubilities, precipitants, &c.), and gives an account of the attempts to isolate and identify the more strongly lævorotatory substance. Its nature, however, is not yet determined.

W. D. H.

Phloridzin-Diabetes. By GRAHAM LUSK (with E. L. MUNSON, E. A. LAWBAUGH, and I. M. HELLER) (*Zeit. Biol.*, 1898, 36, 82—114).—In connection with the question whether the sugar in phloridzin-diabetes originates from proteid or fat, it is pointed out that, from the decomposition of 100 grams of proteid, 45·08 grams of dextrose could

originate. The heat-value of proteid in hunger is 3·8 Cal.; of dextrose, 3·74; the quantity of sugar from proteid would therefore yield 44·1 per cent. of the heat-value of the proteid, which, in phloridzin-diabetes, would be lost to the animal. This would account for the great decomposition of proteid material in these animals. It was hoped that examination of the respiratory quotient would lead to a solution of the question as to whether fat is used up, but the numbers obtained are not sufficiently distinctive for this purpose. W. D. H.

The Experimental Production of Amyloid. By CARL DAVID-SOHN (*Virchow's Archiv.*, 1897, 150, 16—32).—Pure cultures of *Staphylococcus pyogenes* were injected subcutaneously every two or three days into various animals until they died, and in half the cases amyloid degeneration was found. The best results were obtained from cultures prepared from the pus from a case of tubercular empyema. The spleen and bone-marrow showed the change best; then followed liver, intestine, stomach, kidneys, salivary glands, and heart. The pus of the abscesses and the blood of sick and dead animals also contained the same substance. The histological and chemical characters of the new material are very similar to those of the amyloid found in the disease in man. A slight difference in its behaviour to iodine and sulphuric acid is regarded as comparatively unimportant, and the conclusion is drawn that the same disease is being dealt with. W. D. H.

The Experimental Production of Amyloid. By OSCAR LUBARSCH (*Virchow's Archiv.*, 1897, 150, 471—481).—In attempting to produce the disease experimentally in animals, the results have been mainly negative; this is possibly due to want of virulence in the organisms used. Some importance is attached to the difference in colour reactions (especially to aniline dyes) between the artificially produced amyloid and that found in man; this is, perhaps, to be explained by the existence of a hyaline precursor of the amyloid which was found in dogs and rabbits. W. D. H.

Lecithin in Grawitz's Kidney Struma. By GEROLAMO GATTI (*Virchow's Archiv.*, 1897, 150, 417—425).—This growth of the kidney has been variously called lipoma and endothelioma, and by some is regarded as due to suprarenal residues. In order to confirm this view, the amount of lecithin was estimated in two cases, the suprarenal being rich in that substance. In the first of these, the result is regarded as unsatisfactory, because the tumour had been in formalin for a long time. The percentage of lecithin was 0·147 per cent. In the second case, the percentage was 3·47. This is regarded as confirming the view that the growth is of suprarenal origin. W. D. H.

Comparative Examination of the Montecatini Chlorinated Waters. By LUIGI LUCIANI, UBERTO DUTTO, and D. LO MONACO (*Rend. Accad. Linc.*, 1896, [v], 5, ii, 81—93).—The principal springs of chlorinated water at Montecatini, in the Val di Nievole, are those named Tamerici, Torretta, Olivo, Savi, Regina, Acqua media, Villino, and Tettuccio; the medicinal properties of these waters have considerable reputation; they contain chlorides, and act partly as purgatives. By administering definite quantities of the waters to two of the authors

and then determining the chlorides contained in the urine passed during the subsequent five hours, the ratio between the chlorides taken in the water and the chlorine eliminated by the kidneys has been ascertained. This ratio increases as the proportion of chlorides in the water decreases.

W. J. P.

Toxic Action of Acetylene. By UGOLINO MOSSO and FELICE OTTOLENGHI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 324—331).—The authors have made numerous experiments on the toxic action of acetylene on dogs, rabbits, rats, sparrows, frogs, tritons, and newts. The dogs, rabbits, rats, and sparrows were placed in an atmosphere of acetylene, either pure or mixed with air; pure acetylene was also introduced into the lungs of dogs by means of a canula inserted in the trachea. Frogs, tritons, and newts were placed in the gas and in water saturated with acetylene.

The authors conclude that acetylene is highly toxic. The inhalation of 500 c.c. of the pure gas is fatal to dogs unless energetic artificial respiration is resorted to; air containing 20 per cent. of the gas is always fatal to dogs left in it for an hour. Acetylene present in air in small proportion gives rise, in animals, to a period of excitement followed by one of paralysis, during which cardiac and respiratory failure are observed; paralytic symptoms then supervene and death occurs without convulsions.

W. J. P.

Cholesterol and Bile Salts as Chemical Vaccines for Snake Poison. By C. PHISALIX (*Compt. rend.*, 1897, 125, 1053—1055).—The author confirms Fraser's statements as to the antitoxic effect of bile in relation to snake poison. Bile salts and cholesterol have the same effect on viper poison as the bile as a whole, but in both cases this property disappears on heating at 120° for 20 minutes. The bile salts and cholesterol have also a vaccinating, but not an antitoxic, effect. When injected subcutaneously, they confer immunity to snake poison, and this behaviour as a vaccine of a definite chemical compound like cholesterol is particularly noteworthy.

C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Proteolytic Enzyme of Yeast Extract. By MARTIN HAHN (*Ber.*, 1898, 31, 200—201).—The author has succeeded in demonstrating the presence in yeast extract, as obtained by Buchner's method (*Abstr.*, 1897, i, 154, 380), of an enzyme which has the power of rendering albumin soluble. When a few c.c. of the yeast extract is mixed with a few drops of chloroform or any other antiseptic, and then added to solid phenol-gelatin contained in a test tube, an appreciable amount of the gelatin dissolves in the course of 24 hours, and at the end of several days the whole mass has turned liquid. These results are in agreement with those obtained by Schützenberger and by Salkowski on autodigestion, and by Will on proteolytic enzymes in pure yeast cultures (*Centr. Bakt.*, 1896, ii, 92). It is shown that different kinds of yeast yield solutions containing this proteolytic enzyme, and

Neumeister's statement (this vol., ii, 177) that he could obtain no such solution is considered inexplicable. Similar solutions can be obtained from tuberculosis and typhus bacilli. J. J. S.

Detection of the Proteolytic Enzyme of Yeast. By L. GERET and MARTIN HAHN (*Ber.*, 1898, 31, 202—205. Compare preceding abstract).—The yeast extract as obtained by Buchner's method is an opalescent liquid, and even after several filtrations through paper and Kieselguhr filters contains isolated yeast cells. If the solution, which has a somewhat acid reaction, is treated with chloroform and then digested at 37° in a thermostat, a copious precipitate of albumin is deposited in the course of a few hours; at the end of several days, this precipitate has materially diminished, although it has not entirely disappeared, and the liquid is again quite clear. At the end of 2—4 weeks, the amount of precipitate has again reached a maximum, but now consists chiefly of tyrosine crystals; an appreciable amount of leucine may also be obtained by evaporating the mother liquor. Phosphorus appears to be eliminated from the nucleo-albumin after 24 hours, and the small amount of sulphur which occurs in the yeast extract appears to be converted into sulphuric acid. Tables are given showing (1) the gradual disappearance of coagulated albumin, and (2) the gradual increase in the amount of nitrogen in the filtrate when the extract is heated at 37°. J. J. S.

Alcoholic Fermentation without Living Yeast Cells. By EDUARD BUCHNER and RUDOLF RAPP (*Ber.*, 1898, 31, 209—217. Compare Buchner, *Abstr.*, 1897, ii, 154, 380; this vol., ii, 127).—In reply to Stavenagen (this vol., ii, 88 and 177), it is stated that the small numbers of bacteria and yeast cells were not sufficient to account for the large evolution of carbonic anhydride from cane-sugar and the yeast extract. Actual experiments with extract which had been kept for some time so that the zymase was all destroyed, but which still contained living cells, gave practically no carbonic anhydride during the first 40 hours. Stavenagen's criticism that the Berkefeld Kieselguhr filter would not retain yeast spores is considered immaterial, since spores do not occur in the yeast extract obtained from bottom yeast. In reply to von Manassein (this vol., ii, 177), it is stated that a number of her experiments were carried out under conditions which did not admit of complete sterilisation, and other experiments, namely, those in which dried yeast was heated to 300—308° or boiled for 45 minutes and was then shown to be capable of fermentation, must be incorrect, since zymase would be completely destroyed under such conditions. Further experiments with yeast extract have yielded even better results, winter apparently being especially favourable for the production of a strongly active extract.

Zymase differs from most enzymes, for example, invertase, and more closely resembles the substance discovered by Fischer and Lindner (*Abstr.*, 1896, i, 195) in *Monilia Candida*. Zymase diffuses very slowly, if at all, through parchment paper; previous statements regarding its diffusibility are erroneous. Glycogen is readily hydrolysed and fermented by zymase, but not, according to Koch and Hosaeus (*Abstr.*, 1895, ii, 322) by living yeast. This is probably due to the fact that the zymase is enclosed in the cells of yeast, and as glycogen

cannot diffuse through the cell-wall, it thus does not come into contact with the enzyme.

Small quantities of potassium arsenite and carbonate appear to render the yeast extract somewhat more active.

Comparative experiments show that an extract which has been filtered through biscuit porcelain cannot ferment to nearly the same extent as the unfiltered extract. This agrees with experiments made by Sirotonin and by Martin, who have shown that peptone, pepsin, egg-albumin, serum-globulin, &c., are retained by Pasteur's porcelain filter or by a Chamberland's filter the pores of which have been filled with precipitated silica. Probably zymase is also incapable of passing through such filters to any appreciable extent. J. J. S.

Soluble Ferment present in Wine. By GIULIO TOLOMEI (*Real. Accad. Linc.*, 1896, [v], 5, i, 52—56).—Contact with air causes the oxidation of the colouring matter of wine, rendering it insoluble, and developing a characteristic odour; this, according to Martinand (*Compt. rend.*, 1895, 121, 502), is due to the presence of a soluble enzyme, resembling the laccase which Bertrand has isolated from many plants (*Abstr.*, 1895, i, 386; 1896, ii, 61, 571; 1897, ii, 117, 338).

The author finds that the pulp of mature grapes gives, in the air, the characteristic reactions with guaiacum tincture, quinol, and pyrogallol which Bertrand has noted with laccase. After the pulp has been heated at 100°, these reactions are not obtained, and the juice no longer decolorises in the air; these properties are restored to the sterilised pulp by adding the enzyme precipitated by alcohol from a wine must which has not been heated. The soluble ferment dissolves but slowly from the pulp, the latter giving intense colour reactions, whilst the liquor in which it is suspended gives but little colour; successive washings continually extract the ferment from the pulp, and an energetic fermentation favours its solution more than a sluggish fermentation.

On adding a muscatel ferment to a sterilised wine must, the latter after a few days develops a crop of *Saccharomyces ellipsoideus* which, when separated, sterilised, and exposed to the air, gives on extraction with chloroform water, Bertrand's reactions for laccase; similar results were obtained with *Saccharomyces cerevisæ* and *S. apiculatus*.

A young beer yeast was suspended in an aqueous solution of dextrose, alcohol added, and the liquid kept at 0° for 3 days. The liquid was then filtered through a D'Arsonval bougie, and the filtrate, which contained no living organisms, was found (1) to yield hydrogen sulphide with sulphur, (2) to give carbonic anhydride in contact with air, and (3) to absorb oxygen from the air; it also gave the Bertrand colour reactions. All these properties were lost on heating at 72°, and the liquid, on adding alcohol, gave a white precipitate of the enzyme, which, when added to the liquor sterilised by heat, restored to it the properties lost during sterilisation.

The author finds, moreover, that the enzyme may play a part in the maturing of wine. On adding the enzyme extracted from muscatel yeast to an ordinary white wine and exposing it to the air, the wine acquires a muscatel bouquet which it did not previously possess; this

action was hastened by slightly ozonising the air in contact with the wine, and contrasts with the action of organised ferments in that it is greatly promoted by sunlight.

It is concluded that a soluble ferment is elaborated during the development of *Saccharomyces ellipsoideus*, which, remaining dissolved in the wine, is capable of producing all the modifications which constitute the maturing of wine.

W. J. P.

Changes in Fat during Germination. By MAX WALLERSTEIN (*Chem. Centr.*, 1897, i, 63; from *Forsch.-Ber. Lebensm. Bez. Hyg.*, 3, 372—388).—The observations were made on barley during and after softening, and on green malt. The results of examining the ethereal extract are given in tabular form. The most marked change is an increase in free fatty acids and a fall in the amount of neutral fat as germination proceeds. The unsaponifiable constituents markedly increase.

W. D. H.

Dependence of the Respiration of Plants on the Amount of Indigestible Proteids they contain. By WLADIMIR PALLADIN (*Bied. Centr.*, 1897, 26, 753—754; from *Bot. Centr.*, 1896, 67, 79).—Earlier experiments with leaves of *Vicia Faba* showed that the intensity of respiration increases with increase in amount of carbohydrates within certain limits, after which it is about in proportion to the proteids. Only the active proteid of the protoplasm is concerned, and in germinating seeds, in which its amount is comparatively small and varying, there is no definite relation to the respiration.

In the experiments now described, the total and the indigestible proteid nitrogen were determined by Stutzer's method in seedlings of *Triticum* and *Lupinus luteus* growing in darkness; the carbonic anhydride evolved was also determined, and in some cases the amount of soluble carbohydrates. With *Triticum*, the relation CO_2/N_2 was almost constant ($=1.1/1$) and exactly the same as with etiolated leaves of *Vicia Faba*. In the case of lupins, the germinating seeds of which contain but little soluble carbohydrates, the quotient is usually a good deal less, and, moreover, varies according to the degree of germination; the results show, however, that the intensity of respiration, in the case of lupins as with wheat, depends on the amount of indigestible proteid. Contrary to what is usually supposed, the intensity of respiration of wheat continues to increase after the intensity of growth begins to diminish.

During germination in darkness, there is not only a breaking up of proteids, but also a conversion of digestible into indigestible proteids. The author's results, with those of Frankfurt (*Abstr.*, 1894, ii, 113), and of Prianischnikow (*Abstr.*, 1896, ii, 380), show a difference in this respect between oily and starchy seeds, on the one hand, and the more nitrogenous seeds (leguminous) on the other; the former show a considerable increase in indigestible proteids when germinated in darkness, the latter a decrease followed by an inconsiderable increase.

N. H. J. M.

Insoluble Carbohydrates of Wheat. By H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1897, 19, 291—316).—On hydrolysing the carbohydrate matter yielded to boiling dilute acids by vegetable cells from

which the starch has been removed, or hemicellulose from wheat bran, pentoses alone are produced. The product of hydrolysis was brown and of a loose, fibrous texture. On immersion in a solution of ferric chloride and potassium ferricyanide, it fixes a large proportion of ferrous ferricyanide as a deep blue dye, behaving in this respect like a lignocellulose, and when treated with chlorine, the fibrous substance is partially converted into lignone chloride, $C_{19}H_{18}Cl_4O_9$, a compound obtained by Cross and Bevan from chlorinated jute fibre (*Trans.*, 1889, 205).

The cellulose prepared from the fibre by chlorination is apparently not of the normal type; it yields dextrose on hydrolysis, but none of the specific products of hydrolysis of the furfural-yielding group, and on treatment with caustic soda, a substance resembling wood-gum is obtained.

The furfural-yielding compounds constitute one-half of the seed coat exclusive of starch and proteids, and by far the greater part is in the form of easily hydrolysed pentosans.

From experiments on a steer fed with wheat bran only, it appears that the digestibility of the insoluble carbohydrates ranges from 25—100 per cent. The non-nitrogenous extract with a mean digestibility of 76 per cent. is composed of substances whose percentage digestibility varies from 100 to less than 40. Even in the case of the crude fibre, the digestibility of one of the constituents considerably exceeds that of the other. A. W. C.

Raffinose in American Sugar Beet. By WINTHROP E. STONE and W. H. BAIRD (*J. Amer. Chem. Soc.*, 1897, 19, 116—124).—Oxidation with nitric acid fails to detect raffinose when applied to complex mixtures of salts and organic matter, such as molasses. By precipitating molasses from the "crystalliser" of the Norfolk Factory with lead acetate, and oxidising the separated sugars with nitric acid, mucic acid melting at 213° was obtained. This may be regarded as a fairly satisfactory qualitative proof of the presence of raffinose, but nothing short of actual separation of the sugar can be regarded as conclusive.

The authors attempted this isolation in many ways, and by using a method depending on precipitation with lead acetate and strontium oxide, and extraction of the sugars thus obtained with cold methylic alcohol, they obtained fractions having a rotatory power of over 100° , and from this infer that raffinose occurs in the juices of the American sugar beet in appreciable quantities.

Illustrations are given of the appearance of crystals of the various fractions under the microscope, which show that the influence of raffinose is manifested, not in the appearance of isolated raffinose crystals, but in a modified and abnormal appearance of all the crystals. This would seem to afford a ready means of identifying small amounts of raffinose when mixed with sucrose. A. W. C.

Glucosides contained in Digitalis Leaves. By C. C. KELLER (*Chem. Centr.*, 1897, i, 1211). See this vol. ii, 267.

Composition and Nutritive Value of some Edible American Fungi. By LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1898, 1, 225—238).—After giving in full tables the composition (nitrogen and proteid, ether extract, alcohol extract, carbohydrates, crude fibre, ash) of a large number of edible American fungi, the conclusion is drawn that the popular idea of their great nutritive value is a fallacy. It is not unusual to multiply the total nitrogen by 6.25 and express the result as proteid, but even if this is done, and the 75 to 90 of water in fungi allowed for, the amount of proteid is only small. Digestion experiments show that the amount of nitrogenous material not available for nutrition is frequently equivalent to over half of the non-extractive nitrogen present. *Morchella esculenta* is a species of average composition; it contains 10.5 per cent. of solids and 0.48 per cent. of nitrogen; of this, about one-third is extractive nitrogen, and nearly half of the remainder is indigestible. But even if all the nitrogen were present as proteid, the vegetarian would have to consume several kilos. in order to obtain the requisite daily 100 grams of proteid. The fungi are, in fact, inferior in nitrogenous nutritive value to many other fresh vegetables, and although they have a relatively high carbohydrate content, such expressions as "vegetable beefsteak" applied to them are most inappropriate.

W. D. H.

Composition of Well Waters and Soils specially suitable for Tobacco Cultivation in the Charotar, Gujerat. By JOHN W. LEATHER (*Agricult. Ledger*, 1895, No. 14, Calcutta).—A number of well waters, used for irrigating tobacco crops, were analysed, and results obtained which accord with the respective values attached to them by the cultivators. The richest water, taken from a well at Durmuj, contained, N_2O_5 , 1948; Na_2O , 6264; CaO , 92; MgO , 424; SO_3 , 663; and Cl , 4997 per million. This sample contained no potash, but in others the amount of potash was considerable, one sample containing as much as 1098 per million. The value of the waters depends mainly on the amounts of nitrates they contain, and it is estimated that, in the case of very rich waters, an amount of nitrogen may be applied corresponding with 500 lbs. of potassium nitrate per acre.

The soils of which analyses are given are, as is generally the case with Indian soils, poor in nitrogen ($\text{N} = 0.025$ to 0.061 per cent.). The percentage of potash ($\text{K}_2\text{O} = 0.26$ to 0.56) is high as compared with English soils; and the amounts of phosphoric acid (with one exception) are much above the average ($\text{P}_2\text{O}_5 = 0.10$ to 0.42 per cent.).

N. H. J. M.

Recent Experience in the Cultivation of Peaty Land. By BRUNO TACKE (*Bied. Centr.*, 1898, 27, 19—22; from *Mitteil. Ver. Förd. Moorkultur*, 1897, 109).—Experiments in which oats, wheat, and mustard were grown in peaty soil, with and without phosphatic manure, showed that, whilst phosphates increased the yield of oats by 100 per cent., when the soil contained 0.1 per cent. of phosphoric acid, the increase was only 2 per cent. when the soil contained 0.43 per cent. of phosphoric acid. Fleischer found that, with soil containing 0.78 per cent. of phosphoric acid, the addition of phosphates gave better results.

This divergence is probably due to the soil phosphates being in various forms of different value. In peaty soils, the phosphoric acid is in combination with iron, as ferrous ferric phosphate, which is almost equal to basic slag as a phosphatic manure, and as ferric phosphate, which is much inferior. The effect of manuring with phosphates would thus depend on the nature as well as on the amount of the phosphoric acid in the soil.

Superphosphate gave slightly better results than basic slag, but only on the soils poorest in phosphoric acid.

The different potash manures gave very similar results. Potash manures should be applied to peaty soils, partly or wholly in the spring, to avoid loss in drainage.

Experiments made to ascertain the effect of nitrate and of green manuring on the yield of produce are next described. Three soils were used, containing (1) 2.5, (2) 2.86, and (3) 3.39 per cent. of nitrogen, and 5—6 per cent. of lime. The relative amounts of produce without manure were (1) 100, (2) 276, and (3) 384. Sodium nitrate (60 kilos. per hectare) increased the yield as follows: (1) 75, (2) 41, and (3) 26 per cent. With green manuring, the increase was (1) 104, (2) 56, and (3) 26 per cent. The results depend largely on the physical nature of the soil, and the great effect of green manuring (on soil No. 1) is supposed to be due to the porosity of the soil being increased. In cultivating peaty land, the porosity should be increased as much as possible by the growth of deep-rooted plants and by mechanical treatment. Nitrification would thus become more active, and nitrogenous manuring less necessary.

N. H. J. M.

German East African Soils. By FERDINAND WOHLTMANN (*Bied. Centr.*, 1898, 27, 13—14; from *Mitteil. Versuchsfelde landw. Akad. Bonn-Poppelsdorf*, No. 10. Compare Abstr., 1897, ii, 463).—Whilst the soils of Cameroon are very rich, those of German East Africa are less uniformly good, many of them being deficient, especially in phosphoric acid and potash, and some quite unsuited for remunerative cultivation. In some parts, however, the soil is quite equal to that of Cameroon. The presence of luxuriant natural forests is not always an indication of a good soil, and the nature of the vegetation must be ascertained in order to be able to judge as to the value of the land.

N. H. J. M.

Importance of Chemical Analysis of Soils for the Laying out of Plantations. The Soils of Cameroon. By FERDINAND WOHLTMANN (*Bied. Centr.*, 1898, 27, 8—9; from *Mitteil. Versuchsfelde landw. Akad. Bonn-Poppelsdorf*, No. 9. Compare Abstr., 1897, ii, 463).—The object of analysing the soils is to ascertain whether injurious substances are present, and the amount of nutritive matter only. The fine soil which passes through a 2 mm. sieve should be examined, and the determinations should include loss on ignition, nitrogen, and the mineral constituents soluble in hydrochloric acid (*loc. cit.*), the potash, soluble in hot hydrochloric acid, being also determined.

The tropical soils are divided into (1) very rich, (2) good, and (3) poor, according to the amounts of the different constituents they contain. N (1) 0.2, (2) 0.1, (3) 0.05; CaO and MgO, (1) 1.0, (2) 0.4, (3) 0.2; P₂O₅, (1) 0.2, (2) 0.1, (3) 0.06; K₂O (cold extraction) (1) 0.2,

(2) 0.1, (3) 0.05 per cent. The nature of the climate, the amounts of humus, alumina, and ferric oxide and the silica are important, and the geological conditions must be considered. N. H. J. M.

Injurious Effect of Sodium Nitrate. By PAUL WAGNER (*Bied. Centr.*, 1897, 26, 797—800; from *Landw. Presse*, Nos. 18 and 19).—The results of experiments made at Darmstadt showed that perchlorate occurs, as an impurity, in sodium nitrate to the extent of 0.14 to 1.65 per cent. The large amounts, 3 and even 7 per cent., found by Sjollema are probably quite exceptional.

Whilst Sjollema concluded that an application of 200 kilograms per hectare of sodium nitrate containing 0.5 per cent. of perchlorate would be injurious, the author has ascertained that, in ordinary practice, sodium nitrate containing as much as 1.65 per cent. of perchlorate has been found to be without injurious effect.

With regard to the effect of sodium nitrate itself on vegetation, a number of experiments were made in which oats were grown in pots and manured with amounts of nitrate corresponding with 20 to 120 cwts. per hectare. The greatest yield of straw was obtained with 80 cwts. of nitrate per hectare, the yield being very slightly less with 100 and with 120 cwts.; the greatest yield of grain was obtained with the greatest application of nitrate (120 cwts.). The results show that, under the conditions of the experiments, oats will bear a very heavy dressing of sodium nitrate. The nitrate should be applied as uniformly as possible, and only after being finely ground. N. H. J. M.

Analytical Chemistry.

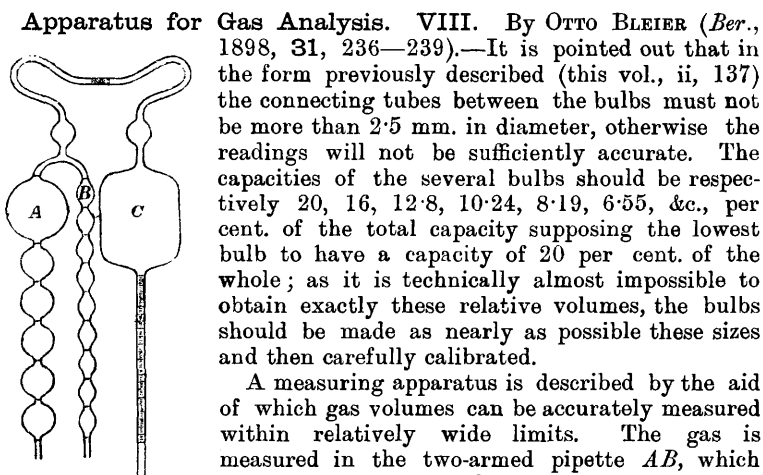


Fig. 1.

A has a capacity of 10 per cent. of the total volume $A + B$, and each

of the nine bulbs of *B* a capacity of 1 per cent. The space between the upper marks in *A* and *B* (that is, the upper bulb and the capillary) has a capacity of 41 per cent. of the total volume. The upper part of *C* has a capacity of 100 volumes, and the graduated tube a capacity of 2.5 volumes. This apparatus is used in pretty much the same manner as that previously described.

As the two-armed measuring tubes with reserve chamber, previously described, cannot always be used for very correct reading, the author has constructed a three-limbed apparatus (see Fig. 2). Each bulb in the limb *B* must have a smaller capacity than *C*, and each bulb of *A* a smaller capacity than *B* + *C*. The three limbs, *A*, *B*, and *C*, together have a capacity = 98.48 c.c., and the capacity of the space between the top marks and the tap = 1.52 c.c., giving a total = 100 c.c.

J. J. S.

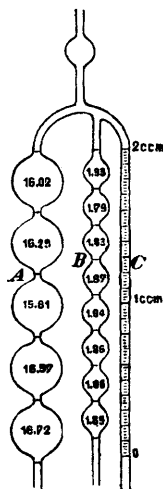


Fig. 2.

Alkalimetry, Acidimetry, and Iodometry, by means of Crystallised Iodic Acid. By E. RIEGLER (*Chem. Centr.*, 1897, 1, 1169—1170; from *Bul. soc. Sciinte*, 6, 37—44).—Pure iodic acid for analytical purposes may be obtained from Merck. Although it may be used with the ordinary indicators, the author prefers adding it in excess and then titrating the uncombined portion with solution of sodium thiosulphate, using starch as indicator. The reaction is represented by the equation $6\text{Na}_2\text{S}_2\text{O}_3 + 6\text{HIO}_3 = 3\text{Na}_2\text{S}_4\text{O}_6 + 5\text{NaIO}_3 + \text{NaI} + 3\text{H}_2\text{O}$. [Compare, however, Walker (this vol., ii, 139).]

L. DE K.

Basic Lead Nitrate as a Clarifying Agent for Polariscope Purposes. By FRANZ HERLES (*Chem. Centr.*, 1897, i, 332—333; from *Zeit. Zuck.-Ind. Böhm*, 21, 189—193).—When using basic lead nitrate, instead of the basic acetate, it is necessary to substitute 143.5 for 144 in the well-known Clerget's formula. For the estimation of saccharose in the presence of raffinose by polarisation before and after inversion, the following formulæ are proposed, $S = \frac{(0.4724 + 0.002t) P - I}{0.9074 - 0.003t}$, and

$R = \frac{P - S}{1.85}$, in which *S* stands for saccharose, *R* for raffinose, *P* for the polarisation before, and *I* for that after inversion, whilst *t* represents the temperature after inversion.

L. DE K.

Estimation of Chlorine, Bromine, and Iodine in Saline Waters. By PERCY A. E. RICHARDS (*Chem. News*, 1897, 76, 293).—In waters where the chlorine is greatly in excess of the bromine and iodine, the total halogens are estimated with decinormal silver nitrate. The iodine is estimated by treating 250 to 500 c.c. with acetic acid and hydrogen peroxide for half an hour, extracting with chloroform, and after the removal of the hydrogen peroxide by washing with water, titrating with decinormal sodium thiosulphate. The bromine is estimated by shaking the solution from which the iodine has been removed

with sufficient chlorine water, extracting with chloroform, washing any chlorine from the extract with water, adding a few crystals of potassium iodide, and titrating with sodium thiosulphate. D. A. L.

Decomposition of Iodine Compounds by Paraldehyde. By WACHHAUSEN (*Chem. Centr.*, 1897, i, 493; from *Pharm. Zeit.*, 42, 95—96).—By the action of paraldehyde on the iodides of sodium, potassium, and iron, the whole of the iodine is liberated. In making use of this reaction as a test for iodine, a little starch paste is added to the solution to be tested and then a few drops of paraldehyde; if iodine is present, the zone of contact of the two solutions becomes red or blue, according to the concentration. Or the solution to be tested may be shaken with paraldehyde, a little starch paste added, and the liberated iodine dissolved in carbon bisulphide. If the solution does not contain more than 1 part of iodine in 500,000 parts, the carbon bisulphide should be repeatedly shaken with fresh quantities of the solution to which the paraldehyde has been added. E. W. W.

Estimation of Sulphuric Acid. By FELIX MARBOUTIN (*Chem. News*, 1897, 76, 232—234).—A critical *résumé* is given of the methods more frequently employed for the volumetric estimation of sulphuric acid, and then the following method is set forth as having particular advantages in water analysis, but is not applicable unless organic matter is absent or has been removed. One hundred c.c. of the water is acidified with hydrochloric acid, boiled to drive off carbonic anhydride, cooled to just below boiling, and treated, drop by drop, with 30 c.c. of a solution of barium chloride containing 4.8 grams of the crystallised salt per litre. After remaining 12 hours at 40°, the solution is neutralised with a few drops of ammonia, treated with 30 c.c. of a solution of potassium chromate (containing 3.9 grams of the crystalline salt per litre), gently heated, then cooled, and made up to 300 c.c. One hundred c.c. of the clear liquid is now treated with 2 c.c. of N/4 sulphuric acid and 5 c.c. of a solution of arsenious acid (prepared by dissolving 4.95 grams of arsenious acid by gently heating with water containing 10 grams of potash, cooling, neutralising with sulphuric acid, and making up to a litre). The mixture is warmed gently, and shaken until completely decolorised, the solution neutralised with potassium carbonate and titrated with a solution of iodine, using starch as an indicator, a corresponding titration is made with a 100 c.c. of distilled water, free from sulphuric acid, and from the difference between the two titrations the amount of sulphuric acid in the sample is calculated. The iodine solution is prepared by dissolving 2.54 grams of resublimed iodine in a solution containing 5 grams of potassium iodide, making up to a litre, and standardising with a known weight of sodium thiosulphate. D. A. L.

Colour Reactions of Nitric and Chloric Acids. By E. C. WOODRUFF (*J. Amer. Chem. Soc.*, 1897, 19, 156—170).—The author has endeavoured to find new tests for nitric and chloric acids which would differentiate between the two, both in mixtures and when other compounds are absent. The latter object has been attained several times, and nitric acid may be detected in presence of chloric acid in

the following manner. A solution of 2 grams of dimethylaniline in 100 c.c. of concentrated sulphuric acid becomes a very strong blood-red when nitric acid alone is added, and brown with chloric acid alone, whilst a mixture of nitric and chloric acids produces only the strong blood-red colour noticed with nitric acid alone.

Details of some hundreds of colour reactions of these two acids with other organic substances are given. A. W. C.

A Volumetric and Gasometric Method of Estimating Hydroxylamine and Hydrazine. By KARL A. HOFMANN and F. KÜSPERT (*Ber.*, 1898, 31, 64—67. Compare *Abstr.*, 1897, ii, 554, 557).—The authors estimate hydroxylamine and hydrazine by oxidation with a dilute solution of vanadic sulphate; the liberated nitrogen is collected and measured, and the vanadylic sulphate produced in the change titrated with potassium permanganate. The solution of vanadic salt is prepared by dissolving ammonium metavanadate in concentrated sulphuric acid and diluting the liquid with water. M. O. F.

Estimation of Phosphorus in Phosphorised Oils. By ANTON SEYDA (*Chem. Centr.*, 1897, i, 560; from *Zeit. öffentl. Chem.*, 3, 13—15).—The author has found that the phosphorus cannot be fully oxidised in the wet way, but that a fusion must be resorted to. To estimate the phosphorus in its solution in olive oil, 30 drops of the sample is put into a 300 c.c. Kjeldahl flask, and 20 c.c. of fuming nitric acid is very slowly added; when the first violent action is over, the flask is heated for 1 hour on the water bath, the bulk of the acid expelled by boiling, the whole diluted with boiling water, and then evaporated to dryness in a platinum dish. Three grams of sodium carbonate and 1 gram of potassium nitrate dissolved in water are then added, and the whole again evaporated to dryness and charred, more nitre being gradually added until a white ash is obtained. The ash contains all the phosphorus as phosphoric acid, which can be estimated by the molybdate process. L. DE K.

Estimation of Phosphoric Acid in Sweet Wines. By WILHELM THÖRNER and R. USTER (*Chem. Centr.*, 1897, i, 825—826; from *Forsch. Ber. Lebensm.*, 4, 55—58).—After criticising the conventional process, and also the method proposed by Glaser and Mühle, the authors recommend the following. Twenty-five c.c. of the sample (if poor in sugar more may be taken and evaporated to 25 c.c.) is heated in a covered beaker with 10 c.c. of strong nitric acid on the water bath for half an hour. Ammonia is added in very slight excess, and then 25 c.c. of ammonium citrate solution; although the liquid becomes much darker, it remains clear. The phosphoric acid is then precipitated by adding 15—20 c.c. of magnesia mixture with constant stirring. L. DE K.

Estimation of Citrate-Soluble Phosphoric Acid. By OTTO REITMAIR (*Chem. Centr.*, 1897, i, 487; from *Chem. Rundsch.*, 1897, 42—43).—The author has found that when 50 c.c. of the conventional solution is poured into a beaker containing 10 c.c. of 10 per cent. sulphuric acid, before adding the conventional magnesium citrate

mixture the precipitate is more crystalline and better fitted for filtering through a Gooch crucible.

L. DE K.

Simultaneous Estimation of Carbon and Nitrogen by Combustion in a Vacuum. By KARL A. H. MÖRNER (*Zeit. anal. Chem.*, 1898, 37, 1—21).—The method of combustion first introduced by Frankland and Armstrong (this Journal, 1868, 87—101) and subsequently very fully described in Sutton's *Volumetric Analysis*, is especially suitable for the analysis of organic substances of which only small quantities are available. The author has introduced but few modifications, the most important being the mixing of the substance with moist cupric oxide, and the expulsion of the water by heating the combustion tube in a water bath during the exhaustion before combustion. By this means, the residual air is so completely expelled that in the analysis of a non-nitrogenous substance only a few hundredths of a cubic centimetre of nitrogen are obtained. The substance is mixed with the cupric oxide in a mortar, and mixing must be very intimate. As the use of a copper spiral rarely effects the complete reduction of the nitric oxide, which must therefore always be sought for and measured, there is no advantage in inserting one. Combustible gases (CO , H_2 , C_2H_6 , C_2H_4 , and C_2N_2), varying in quantity and composition according to the substance burnt and the rate of heating, are almost invariably present, and must be exploded with oxy-hydrogen gas and estimated by the usual methods of gas analysis. Although substances containing 27 per cent. of sulphur were analysed by this method, no error was introduced by its presence and no sulphurous anhydride was ever found in the gases. The errors in a series of analyses ranged from +2.5 to -1.1 per cent. of the carbon present, and +2.3 to 1.4 per cent. of the nitrogen, but the mean error was only 0.7—0.8 per cent.

M. J. S.

Combustion of Organic Substances by Wet Methods. By ISAAC K. PHELPS (*Zeit. anorg. Chem.*, 1898, 16, 85—98).—The method is based on the iodometric estimation of carbonic acid previously described by the author (*Abstr.*, 1896, ii, 673). Oxalic, formic, and tartaric acids and other easily oxidisable compounds are oxidised by potassium permanganate and the carbonic anhydride is absorbed in barium hydroxide solution, the excess of barium hydroxide being determined as previously described. Compounds which are difficult to oxidise and compounds like the carbohydrates which, when oxidised with chromic and sulphuric acids, yield a mixture of carbonic anhydride and carbonic oxide, are oxidised with a mixture of potassium dichromate and sulphuric acid in a closed flask so that any carbonic oxide which is formed is converted into carbonic anhydride by the prolonged action of the oxidising agent. The substance, enclosed in a sealed tube of thin glass, is brought into the oxidising flask, which, by means of a glass tube fitted with a tap, is connected with the flask containing the barium hydroxide. The air is expelled by boiling both the water in the oxidising flask and the hydroxide solution in the other flask; the flasks are then closed from the air and from each other, and the mixture of potassium dichromate and sulphuric acid is admitted to the oxidising flask through a separating funnel. The oxidation is effected

by heating at 105° , and the carbonic anhydride is then driven over into the barium hydroxide by boiling the solution.

The oxygen in many organic compounds can be determined by using a weighed quantity of potassium dichromate in the above method, and after the oxidation is complete determining the excess of the oxidising mixture employed by treating the residue with hydrochloric acid, absorbing the chlorine evolved in a standard solution of alkali arsenite, and titrating the excess of arsenite with iodine solution.

This method is not applicable to substances which are both difficult to oxidise and very volatile.

E. C. R.

Detection of Sodium Hydrogen Carbonate in Milk. By LÉON PADÉ (*Chem. Centr.*, 1897, i, 337; from *Ann. chim. anal. appl.*, 1886, 1, 328).—The soluble portion of the ash obtained from 10 grams of milk only requires one drop of N/10 sulphuric acid for neutralisation, but if the sample contains sodium hydrogen carbonate, much more acid will be required. In this case, it must be remembered that part of the added soda may have been converted into phosphate. An estimation of the soluble phosphoric acid should, therefore, not be omitted, and this must be calculated into the corresponding amount of sodium hydrogen carbonate.

L. DE K.

Estimation of Zinc in Foods. By JANKE (*Chem. Centr.*, 1897, i, 519; from *Zeit. Nahrungsm. Hyg. Waar.*, xi, 25—26).—To 50 to 100 grams of the sample which has been cut up into small pieces, dried for 3 hours at 125° , and then powdered, 25 c.c. of nitric and 10 c.c. of sulphuric acid are added; after the first violent action is over, the acid is evaporated and the residue incinerated to a white ash. This is dissolved in nitric acid, the excess of acid removed by evaporation on the water bath, the residue dissolved in water, filtered, and the filtrate neutralised with sodium carbonate; any iron present is precipitated as phosphate by means of sodium acetate, and the zinc is then precipitated as sulphide by hydrogen sulphide.

L. DE K.

Electrolytic Separation of Cadmium and Zinc, Zinc and Cobalt, and Antimony and Tin. By A. WALLER (*Zeit. Elektrochem.*, 1897, 4, 241—247).—*Zinc and Cadmium.*—A neutral solution of the chlorides in 120 c.c. of water is treated with 8 grams of potassium oxalate and 2 grams of ammonium oxalate and electrolysed at $80-85^{\circ}$. Since the E. M. F. required for the decomposition of the zinc salt is about 0.3 volt higher than that required for the cadmium salt, and the resistance of the electrolytic cell employed was 10 ohms, it follows that a current not exceeding 0.03 ampère will deposit the cadmium and not the zinc. With 0.02 ampère, the deposit of cadmium was smooth and free from zinc. The test analyses given show that the method yields excellent results.

Zinc and cobalt were separated by the method described by Vortmann (*Elektrochem. Zeit.*, 1, 6). Cobalt potassium sulphate and zinc ammonium sulphate were dissolved in water, 6 grams of Rochelle salt, 1 to 1.5 grams of potassium iodide, and 2 to 3 grams of caustic soda added, and the whole made up to 150 c.c. and electrolysed at $60-65^{\circ}$ with about 2 volts and 0.05 to 0.1 ampère. A little cobaltic oxide

Co_2O_3 , is deposited on the anode which must be weighed after drying at 110° . The error of the determinations does not exceed 1 per cent. of the cobalt present.

Antimony and tin are separated by Ost's method. The antimony and tin salts are dissolved in 120 c.c. of a solution containing pure sodium sulphide (quantity not stated) and 2—3 grams of sodium hydroxide, and electrolysed at 60° . From the author's experiments, it follows that, under these circumstances, antimony free from tin is deposited when the E. M. F. employed varies between 0.45 and 0.7 volt. When the E. M. F. exceeds 0.7 volt, tin is deposited along with the antimony.

T. E.

Estimation of Copper in the Presence of Other Elements.
By HARRY BREARLEY (*Chem. News*, 1897, **76**, 291—293, 303—304).—The author has applied his modifications of the cyanide titration of copper (this vol., ii, 140) in the presence of various elements, using in each case 0.10 gram of copper; alkali salts, equivalent to 20 c.c. of hydrochloric acid (twice normal strength) as chloride; excess of sodium carbonate, 30 c.c. (2N); excess of ammonia, 10 c.c. (2N). Sodium, potassium, magnesium, molybdenum, arsenic, antimony, bismuth, lead, and uranium cause no appreciable error. Zinc causes various difficulties, requires more ammonia, also more cyanide, and then reacts with the silver nitrate, so that it is best to add an excess of that reagent, filter, and titrate the excess with cyanide; or sodium pyrophosphate in concentrated solution may be added to both the solution and the standard copper, when fairly good results are obtained; the same reagent may be used in the presence of cadmium, although it is scarcely required in that case, but it is said to be useful in the presence of iron. With aluminium, the precipitates with ammonia or sodium carbonate are objectionable, and must be stopped by making alkaline with soda or potash, or by the use of sodium pyrophosphate, or a system of fractional filtration must be adopted, adding the bulk of the silver nitrate required before the filtration. The use of soda or potash is only to be recommended within narrow limits, not more than 10 c.c. of 2 normal soda in about 250 c.c. of solution. Neither citric nor tartaric acid can be used. With iron, the ammonia, the results are good, those with soda, bad. Manganese, in the ordinary way, forms a double salt with copper, and so gives low results; this can be obviated by adding sodium carbonate to the acid solution of copper and manganese until a slight precipitate forms, dissolving in a slight excess of acid, adding cyanide and then the usual excess of sodium carbonate; the approximate amount of copper must be known, as there are no distinctive colour changes, the last precipitate must not be filtered until it has changed from the white, crystalline to a brownish, granular, powdery, and more compact condition. Chromium as chromic oxide is harmful, as chromic acid it is harmless. Cobalt, nickel, silver, gold, palladium, and platinum have not been tried. Mercury exerts an influence that is fairly regular, as might be expected from Denigès' experience (*Abstr.*, 1897, ii, 433). The precipitation of copper by means of sulphurous acid and potassium thiocyanate is satisfactory, but filtration is a difficulty; the author's recommendation, therefore, is to decant the solution on to

a small asbestos or paper pulp filter, wash, if necessary, with a dilute solution of the reagents; return to the precipitating vessel, add a few c.c. of nitric acid and 20 c.c. (2N) hydrochloric acid, boil for a few minutes, cool, neutralise with sodium carbonate, add the usual excess, and titrate.

D. A. L.

Estimation of Copper as Iodide. By WILLENZ (*Chem. News*, 1897, 76, 243—244).—The author employs an approximately N/25 solution of sodium thiosulphate which is standardised with metallic copper and verified before each set of analyses; the method used for this purpose must be rigorously followed in the actual analyses, and is as follows. Ten grams of electrottype copper is dissolved in equal volumes of water and nitric acid, sp. gr. = 1.4, the nitrous fumes are expelled by boiling, and the solution diluted to a litre. Ten c.c. of this solution is transferred to a 200 c.c. conical flask with a mark at 50 c.c., and carefully treated with dilute ammonia until precipitation ceases; dilute acetic acid is then gradually added to dissolve the precipitate, and this solution is made strongly acid with 5 or 6 c.c. of concentrated acetic acid, diluted to 50 c.c., and mixed with 10 c.c. of a 10 per cent. solution of potassium iodide, which is allowed to react exactly 2 minutes. The thiosulphate solution is now run in until a clear, yellowish-brown tint is attained; a small quantity of starch solution is next added, and the addition of thiosulphate continued with agitation until the colour changes to dirty greyish-violet, when the thiosulphate is added in drops, agitating vigorously after each drop; the appearance of a straw colour is taken as the end of the titration.

It is also applicable to pyrites, the preliminary treatment of the mineral being as follows. Ten grams of finely powdered and dry pyrites, with 8 c.c. of water and 2 c.c. of sulphuric acid, is treated gradually with from 25 to 30 c.c. of nitric acid, sp. gr. = 1.4, until there is no further effervescence, when another 3 c.c. of sulphuric acid is added. The whole is boiled, agitating meanwhile until pasty, treated with hot water, boiled again for a short time, cooled, diluted to half a litre, and filtered. One hundred c.c. of the filtrate is treated with a few c.c. of sulphuric acid, and while boiling, a warm, concentrated solution of sodium thiosulphate is gradually added; the solution assumes various colours, ultimately becoming black, but the boiling is continued until the precipitate agglomerates. The precipitate is washed rapidly several times with boiling water, by decantation and on the filter, until free from sulphuric acid, pressed between blotting paper, and gently heated in a crucible to get rid of moisture; finally, heated strongly to eliminate any sulphur, arsenic, antimony, and tin. The residue is dissolved in 1 c.c. of a mixture of equal volumes of water and nitric acid, sp. gr. = 1.4, and the process continued in the manner described above.

D. A. L.

Separation of Mercuric from Bismuth Salts. By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1898, 31, 129—130. Compare *Abstr.*, 1897, ii, 604).—Mercury and bismuth can be readily and accurately estimated in mixtures of the two by adding a mixture of hypophosphorous acid and hydrogen peroxide to the solution slightly acidified with hydrochloric acid, when the mercury is precipitated as calomel.

The filtrate is then made faintly alkaline with caustic soda, warmed to remove the hydrogen peroxide, and treated with more hypophosphorous acid, which precipitates the bismuth in the metallic state. A. H.

Estimation of Nickel in Iron, Cast Iron, and Steel. By PERILLON (*Chem. Centr.*, 1897, i, 437; from *Rev. chim. anal. appl.*, 5, 21—22).—A quantity varying from 0.25 to 4 grams of the sample is dissolved in nitric acid of sp. gr. = 1.2, and after the excess of acid has been expelled by boiling, enough aqueous potash is added to precipitate the metals; 25 grams of oxalic acid is then added, and the whole dried at 80°. On boiling the dried mass with 100 c.c. of a mixture of equal volumes of water, acetic acid, and alcohol for some time, and finally keeping for 4 hours at 80°, the nickel oxalate is completely precipitated and may be obtained free from alkalis by washing it with a 10 per cent. solution of oxalic acid. On ignition, it leaves nickel oxide, which may be freed from traces of iron and manganese by dissolving it in hydrochloric acid, and then adding bromine water and ammonia; the precipitate containing the iron and manganese is weighed and the necessary correction made. L. DE K.

Estimation of Chromium in Iron Chromium Alloys. By HEINRICH FRESENIUS and H. BAYERLEIN (*Zeit. anal. Chem.*, 1898, 37, 31—35).—The greater part of the alloy employed was soluble in hydrochloric acid. The solution was evaporated to remove silica; the small portion not soluble was fused in a silver crucible with sodium peroxide, by which means all the chromium it contained was rendered soluble as chromate, and was united with the principal solution, which was then treated with an excess of sodium peroxide and digested at a gentle heat until evolution of gas ceased. The precipitated ferric oxide was redissolved and once more treated with sodium peroxide, and was then perfectly free from chromium. The main alkaline solution was next acidified with hydrochloric acid, treated with hydrogen peroxide, boiled until the peroxide was decomposed and the chromate reduced, and evaporated to dryness to get rid of silica dissolved from the glass vessels. After redissolving in acid, it was precipitated with ammonia in a platinum dish, and the precipitate of chromic oxide weighed. To remove traces of alumina, it was fused with alkali carbonate and nitrate, and the solution precipitated by ammonia and ammonium carbonate. The precipitate was not free from chromium, and required a repetition of the fusion, &c.

For the qualitative detection of iron, aluminium, and chromium, it is sufficient to free the solution from excess of acid, add excess of sodium peroxide, and heat; filter from the iron precipitate and test for alumina by ammonia after acidifying with hydrochloric acid.

M. J. S.

Thorium Hydrogen Oxalate. By CHARLES GLASER (*Zeit. anal. Chem.*, 1898, 37, 25—28).—A further examination of the salt precipitated by hydrochloric acid from a solution of thorium oxalate in ammonium oxalate shows that it has not the simple composition previously assigned to it (*Abstr.*, 1897, ii, 349), but is a mixture of the normal and the acid oxalate, the composition varying somewhat

according to the circumstances under which it is precipitated. The analyses made are not quite conclusive, but when the amount of the normal salt ($\text{ThC}_2\text{O}_4 + 2\text{H}_2\text{O}$) calculated from them was deducted, the remainder indicated for the acid salt the formula $\text{Th}_2\text{H}_2(\text{C}_2\text{O}_4)_5 + 9\text{H}_2\text{O}$, after drying at 115° .
M. J. S.

Volumetric Estimation of Antimony. By FERDINAND GAUTIER (*Actes Soc. Sci. Chili*, 1897, 7, 74—76).—See this vol., ii, 232.

Estimation of Carbonic Anhydride in Natural Waters. By CLARENCE A. SEYLER (*Analyst*, 22, 312—316).—The author has made use of Trillich's process for the last seven years and again recommends it as being quite trustworthy. One hundred c.c. of the sample is mixed with a few drops of a neutral alcoholic solution of phenolphthalein and titrated in a narrow glass cylinder with a N/20 solution of sodium carbonate, until a faint, but permanent, red tint appears. This gives the free carbonic anhydride alone. The combined acid is then estimated by adding a little methyl-orange and titrating with N/20 hydrochloric acid; the total carbonic acid is the sum of the two titrations. Water, which, after boiling, turns red with phenolphthalein does not necessarily contain alkali carbonates, as the red coloration may be due to incompletely precipitated calcium or magnesium carbonate.

Attention is called to the great importance of the free and half-bound carbonic acid when Clark's softening process is to be applied.

L. DE K.

Estimation of Paraffin in Petroleum of High Boiling Point. By D. HOLDE (*Chem. Centr.*, 1897, i, 309, 443; from *Chem. Rev. Fett u. Harz. Ind.*, 4, 4—6, 21—25).—The author considers the processes of Pawlewski and Filemonowicz, Zaloziecki and Höland, Höland and Aisinmann as untrustworthy, and recommends the following: 10—20 c.c. of a sample solidifying at -5° , or 5 c.c. of a sample solidifying at 0° , is dissolved in the smallest amount of a mixture of equal parts of commercial absolute alcohol and ether. This solution, contained in a 200 c.c. Erlenmeyer flask, is cooled to -18° or -20° by a mixture of ice and salt, and more alcohol-ether mixture is cautiously added until no more oil-drops are visible and there is merely a flocculent deposit of paraffin. The liquid is then filtered, the funnel being surrounded with a freezing mixture, and washed with the ether mixture cooled to -20° if dealing with hard paraffin, but for soft paraffin a mixture of 2 vols. of alcohol and 1 vol. of ether cooled to -20° is used. The washing is continued until 10 c.c. of the filtrate no longer gives an oily residue. The insoluble residue is dissolved off the filter by hot benzene, which is then evaporated in a tared beaker. When dealing with a product rich in soft paraffin, it is necessary to treat the residue once more in the manner described above.

Petroleum containing pitch or asphalt cannot be tested by this method.

L. DE K.

Estimation of Paraffin in Crude Oil Distillates. By SEMJON AISINMANN (*Chem. Centr.*, 1897, 1, 1261—1262; from *Chem. Rev. Fett u. Harz. Ind.*, 4, 106—108, 117—119).—The author states that paraffin is quite insoluble in absolute alcohol cooled down to -15° by means

of a mixture of ice and salt. Five grams of the sample dissolved in a sufficiency of absolute alcohol is cooled to -15° ; when no more paraffin separates, the liquid is filtered off through a funnel surrounded by a freezing mixture, and the filter is washed with absolute alcohol at -15° until the washings no longer become turbid on adding water. The paraffin is then dried in a desiccator and weighed. L. DE K.

Tabarie's Method for the Estimation of Alcohol. By NORMAN LEONARD and HARRY M. SMITH (*Analyst*, 22, 225—227).—In this process, the sp. gr. of the alcoholic liquid is taken; a known volume is then evaporated to a small bulk to drive off the alcohol, and after making up to the original bulk with water, the sp. gr. is again taken. To get the sp. gr. of the spirit, either the extract gravity is divided into the present gravity, or the excess of extract gravity over 1000 is deducted from the present gravity. There having been much discussion as to which of the two calculations is the correct one, the authors have made a long series of experiments on the subject, and have come to the conclusion that, for spirits with but little solid matter, the division formula should be used, whilst the subtraction formula should be employed for heavily sweetened articles. L. DE K.

Behaviour of Glycerol towards Metallic Oxides with a view to its Quantitative Estimation. By FRIEDRICH BULLNHEIMER (*Chem. Centr.*, 1897, 1, 522—523; from *Forsch. Ber. Lebensm.*, 4, 12—21).—This is an account of a series of experiments, not yet finished, on the solubility of metallic oxides in glycerol containing excess of free alkali. The only oxides which dissolve to a considerable extent are those of copper, bismuth, and antimony. The following six oxides are completely reduced to the metallic state under the conditions of experiment, namely, silver, gold, mercury, rhodium, palladium, and platinum. L. DE K.

Detection of Glycerol. By GEORGES DENIGÈS (*Chem. Centr.*, 1897, 1, 1002—1003; from *Bull. Soc. Pharm. Bordeaux*, 36, 356).—The glycerol is first isolated by the well-known method of extraction with alcohol-ether, and after evaporating the latter, the residue is heated in a small retort with potassium hydrogen sulphate. If a pungent odour of acraldehyde is emitted, a rod moistened with Nessler's reagent, or an ammoniacal silver nitrate solution is exposed to the fumes; when acraldehyde is present, the reagent will become brown. L. DE K.

Detection of Picric Acid, and Distinction from Dinitrocresol (Saffron Substitute). By A. RYMSZA (*Zeit. anal. Chem.*, 1897, 36, 813—814; from *Inaug. Dissert. Dorpat*).—The substance is macerated for several hours with water acidified with sulphuric acid, then mixed with 3 vols. of 95 per cent. alcohol, and digested for 24 hours at $50-60^{\circ}$. After filtration and evaporation of the alcohol, any fat is removed by shaking with light petroleum, and the liquid is then acidified with hydrochloric acid, and shaken repeatedly with ether. Urine, which in cases of poisoning with picric acid is always coloured reddish-brown by the presence of picramic acid, may be extracted with ether after simply acidifying. The residue obtained by evaporating the ether is then tested for picric acid, by (1) the isopurpuric acid reaction (blood-red colour on warming with potassium cyanide and soda),

(2) the picramic acid reaction (blood-red colour on heating with soda and grape-sugar), or, better, (3) soda and ammonium sulphide, (4) ammoniacal copper solution (yellowish-green precipitate of hexagonal needles which polarise light), and (5) by dyeing white wool. The limit of sensitiveness of the five reactions is 1:5000, 1:7060, 1:12500, 1:80000, 1:110000 respectively. Reactions (2) and (5) are less sensitive in presence of fats and other substances.

When reduced with stannous chloride and hydrochloric acid, potassium dinitrocresol gives a cherry-red colour with ammonia; picric acid, a brownish-red. Reduced with zinc and hydrochloric acid, the former gives a bright red colour, which disappears after a time. Picric acid sometimes gives a blue colour, later a brownish-green, which remains unchanged for days.

M. J. S.

Detection of Cholesterol and Phytosterol in Fats. By ARTHUR FORSTER and RUDOLF RIECHELMANN (*Chem. Centr.*, 1897, i, 563; from *Zeit. öffentl. Chem.*, 3, 10—12).—The sample (50 grams) is boiled twice for 5 minutes with 75 c.c. of 96 per cent. alcohol, using a reflux condenser, and when cold the spirit is decanted off through a filter. The filtrate is then heated in a retort with 50 c.c. of 50 per cent. aqueous soda until about three-fourths of the spirit has distilled over, the residue transferred to a porcelain dish, and the rest of the spirit removed by evaporation. The aqueous liquid is then extracted by shaking with ether in a suitable apparatus, the ethereal liquid distilled to dryness, and the residue again taken up with a little ether, which is filtered into a small glass and allowed to evaporate slowly. The residue is again dissolved in strong alcohol and allowed to crystallise, when it will be in a sufficiently pure condition for microscopical examination, best with polarised light.

Cholesterol crystallises in very thin, rhombic tablets. Phytosterol, on the other hand, in fascicular, well-formed, fairly broad needles; when crystallised very slowly, the crystals assume the form of six-sided tablets. From undoubtedly pure lard, the authors have sometimes obtained crystals of cholesterol which were not well formed, so as to render the test uncertain.

L. DE K.

Fehling's Solution. By J. BISHOP TINGLE (*Amer. Chem. J.*, 1898, 20, 126—127).—Since ordinary Fehling's solution, unless strongly alkaline, is reduced by mineral acids (compare Jovitschitsch, this vol., ii, 98), the use of the following solution, described by Purdy, is recommended. 4.742 grams of crystallised copper sulphate is dissolved in 200 c.c. of water and 38 c.c. of glycerol, and mixed with 23.5 grams of potassium hydroxide dissolved in 200 c.c. of water; 450 c.c. of ammonia (sp. gr. = 0.9) is added, and the mixture diluted to 1 litre; 35 c.c. of this solution is equivalent to 0.02 grams of dextrose; to determine dextrose, 35 c.c. of the copper solution is diluted with 70 c.c. of water, boiled, and the sugar solution added, drop by drop, until the blue colour is discharged. The copper solution is not reduced by mineral acids, and is unchanged by long keeping.

W. A. D.

Estimation of Dextrose. By EDUARD PFLÜGER (*Pflüger's Archiv.*, 1898, 69, 339—471).—A critical article dealing with the various

methods of estimating sugar, and giving full details of a new method, a preliminary notice of which has already appeared (*Abstr.*, 1897, ii, 378).
W. D. H.

Volumetric Estimation of Grape Sugar and other Substances Oxidisable by Fehling's Solution. By E. RIEGLER (*Zeit. anal. Chem.*, 1898, 37, 22—25).—The method depends on the use of an excess of the Fehling's solution and the titration of the excess of copper by iodine and thiosulphate. Ten c.c. of standard copper sulphate (69.28 grams per litre) is mixed with 10 c.c. of the alkaline tartrate solution (346 grams of sodium potassium tartrate and 100 grams of sodium hydroxide in the litre), and 100 c.c. of water; 2 c.c. of pure concentrated sulphuric acid is added and well mixed in, the mixture is cooled, 1 gram of potassium iodide in 10 c.c. of water is added and a little starch, and the liberated iodine is titrated with N/10 thiosulphate until the blue colour is destroyed and does not reappear for 5 minutes (a reappearance later is to be disregarded). If the thiosulphate is of correct strength, 27.8 c.c. will be required, and each c.c. will correspond with 0.00635 gram of copper.

Fresh quantities of the copper and tartrate solutions diluted with 30 c.c. of water are heated to boiling, 10 c.c. of the sugar solution, which must not exceed 1 per cent. in strength, is run in, and after boiling for a few seconds the precipitated cuprous oxide is filtered off with a dense filter and well washed. The filtrate is acidified and titrated as above, and from the difference between the two titrations the copper precipitated is calculated, and the corresponding amount of grape sugar found from Allihn's table. Test analyses showed satisfactory results. For the estimation of lactose in milk, the proteids must be first removed. This is very neatly effected by using a solution of asaprole in citric acid (30 grams of each per litre); 15 c.c. of this reagent suffices for 10 c.c. of milk, the mixture being made up to 100 c.c., warmed to 60°, and filtered. Twenty c.c. of the filtrate is then treated with the mixed copper solutions as before, the boiling being continued for 6 minutes before filtering. Soxhlet's table gives the amount of lactose corresponding with the copper precipitated.
M. J. S.

Detection and Estimation of Saccharose in Wine. By ARTHUR BORNRÄGER (*Zeit. anal. Chem.*, 1897, 36, 767—776).—Saccharose is always detected and estimated by inverting with an acid and ascertaining the increase in lævorotation of polarised light and in reducing power, but the proportion of acid to be used, and the time and temperature of heating have been most variously prescribed by different authorities. Of late, the opinion seems to have gained ground that with the large quantity of acid employed by the early experimenters a danger existed of partially reversing the lævorotation of the inverted sugar (compare Bishop, *Abstr.*, 1889, 85). The author confirms the fact of this reversal when the heating is unduly prolonged, but shows that with sugar solutions of the strength employed for Soleil's instrument (16.35 grams per 100 c.c. and stronger solutions are hardly ever met with among sweet wines) the maximum lævorotation is attained when 1/10 volume of hydrochloric acid of sp. gr. = 1.1 (20 per

cent.) is added and the temperature is maintained at 67—70° for 10—20 minutes. With the Ventzke solution, however (26·048 grams per 100 c.c.), the maximum is reached at 10 minutes and already at 15 minutes a falling off is observed. The author therefore regards the method which he adopted in 1888 (*Abstr.*, 1890, 426) as free from all objection, especially when it is considered that many hundred samples of sweet wine free from saccharose examined by this method have given practically identical rotations before and after inversion. When the saccharine strength does not exceed that of the Soleil standard, inversion may be completed by leaving the mixture for 18 hours at 18—20°, but with the stronger solution, it is incomplete even at 48 hours. Sweet wines free from saccharose show a slight increase (2·2 degrees Ventzke with a 200 mm. tube) when inverted in the cold, although the reducing power remains unchanged, and since 1 degree Ventzke of laevorotation corresponds with about 0·8 gram of saccharose per 100 c.c. the measurement of the reducing power after cold inversion is the more accurate method of estimating the saccharose present.

M. J. S.

Estimation of Glycogen in the Liver. By A. E. AUSTIN (*Virchow's Archiv.*, 1897, 150, 185—196).—Brücke's method of preparing glycogen leaves a considerable quantity of that substance in the liver, which can be then extracted by Külz's method. Various objections to the use of the latter method are, however, advanced. A method was therefore devised in which the liver was first subjected to gastric digestion; the amount then obtained was sometimes more, sometimes less, than by Külz's method. Pepsin hydrochloric acid has no action on glycogen.

W. D. H.

Detection of Aldehydes and Phenols. By BARBET and JANDRIER (*Zeit. anal. Chem.*, 1898, 37, 47—48; from *Ann. Chim. anal.*, 17, 325).—A few c.c. of a phenol are mixed in a test tube with 2 c.c. of absolute alcohol containing traces of an aldehyde, 1 c.c. of concentrated sulphuric acid is then poured down the side, and the colours observed at the contact surface and after shaking.

With phenol and acraldehyde (a 0·001 per cent. solution), the acid layer is yellow, the alcoholic violet. On shaking, the whole becomes heliotrope-coloured.

Formaldehyde gives no such reaction with phenol; but with gallic acid the lower layer is yellow and the upper blue, and, on shaking, the whole becomes heliotrope-coloured, passing into salmon colour, or with a stronger solution (0·01 per cent.), dirty green. Acraldehyde gives no colour with gallic acid. β -Naphthol, α -naphthol, quinol, and phloroglucinol all give colours with aldehydes, some of the reactions being both characteristic and very sensitive.

M. J. S.

Detection of Chloral Hydrate. By ADAM JAWOROWSKI (*Zeit. anal. Chem.*, 1898, 37, 60—61; from *Pharm. Zeit. Russ.*, 33, 373).—A solution of 0·12 gram of resorcinol in dilute aqueous chloral hydrate poured upon dilute sulphuric acid gives a brown ring at the contact surface, and the whole becomes brown on shaking. Strong ammonia floated on the mixture acquires a yellowish-red colour. Aqueous

chloral hydrate gives, with Nessler solution, a brick-red precipitate, changing to dirty yellowish-green. Chloral hydrate solution (2 c.c. containing 0.03—0.06 gram) when boiled with 0.3 gram of potassium thiocyanate, and then treated with 3—5 drops of normal potash solution, becomes light brown, and on standing gives a dark brown precipitate with a colourless upper liquor.

A similar experiment with 0.2—0.3 gram of sodium thiosulphate gives a turbid, brick-red liquid, becoming clear and brownish-red when the potash is added. When phloroglucinol is heated with chloral hydrate and then treated with potash, it gives a deep brown-red colour; on acidifying with hydrochloric acid after cooling and then shaking with amylic alcohol, the latter becomes brownish-red.

M. J. S.

Estimation of Acetic Acid in the Presence of Inorganic Salts. By BERTRAM BLOUNT (*Analyst*, 22, 309—310).—The mixture, which should be free from nitrates, is distilled with dilute sulphuric acid until fumes of the latter begin to make their appearance, the distillate being collected in a receiver containing aqueous soda. It is then evaporated nearly to dryness, and a large excess of absolute alcohol added, which dissolves the sodium acetate and the excess of sodium hydroxide, leaving the sodium chloride and sulphate as an insoluble residue. As the solution still contains some impurities, the alcohol must be evaporated, and the residue re-distilled with dilute sulphuric acid; the distillate is collected in a receiver containing aqueous baryta, and after the excess of baryta has been removed by means of carbonic anhydride, the barium acetate is dried and weighed.

L. DE K.

Dissociation of the Salts of Petroleum Acids and the Estimation of Free Acids in Mineral Oils. By ROMAN ZALOZIECKI (*Chem. Centr.*, 1897, i, 444; 524—525; *Chem. Rev. Fett. u. Harz. Ind.*, 4, 25—27; 36—38).—The author states that the free acidity of mineral lubricating oils is best estimated by means of N/10 soda dissolved in proof spirit.

The soap formed is not decomposed by water, but is hydrolysed to a certain extent when agitated with petroleum.

L. DE K.

Detection of Margarine. By HERMANN BREMER (*Chem. Centr.*, 1897, i, 948; from *Milch. Zeit.*, 26, 210—211).—It has been proposed to add small quantities of phenolphthalein or dimethylamidoazobenzene to margarine so as to facilitate its detection; the addition of 5 per cent. of sesame oil is recommended by the author, who wishes this to be made compulsory, not only in the case of butter substitutes, but also for lard adulterants.

L. DE K.

Rapid Detection of Margarine in Cheese. By RUDOLF HEFELMANN (*Chem. Centr.*, 1897, i, 1002; from *Zeit. öffentl. Chem.*, 3, 117—120).—Twenty to 50 grams of the rasped cheese is introduced into a tube 20 cm. long and 2.5 cm. wide; 20—25 c.c. of hydrochloric acid of sp. gr. = 1.19 is added, and the tube is then placed in a boiling water bath for about half an hour; the casein dissolves, and the fatty matter floats on the top of the brown liquid. A few drops of the fat

are then pipetted off and tested in the butyro-refractometer. If the fat which separates is not quite clear, it must be dissolved by agitating the liquid with light petroleum, when the latter, on evaporation, will leave the fat in a sufficiently pure state.

L. DE K.

Examination of Cheese for Foreign Fats (Artificial Cheese) and the Estimation of Water and Fat in Cheese. By ARTHUR DEVARDA (*Zeit. anal. Chem.*, 1897, 36, 751—766).—The estimation of the volatile fatty acids by the Reichert-Meissl process is a most valuable method of detecting the presence of foreign fats. Although in most cases the true milk fats of cheese show little change after the completion of the ripening process, yet, in consequence of the development of lactic acid and of certain unelucidated changes in the proteids, the fats extracted by ether often show a higher percentage of volatile fatty acids than is the case in butter. The following method of extraction avoids this source of error. About 50—100 grams of the cheese, cut into small fragments or rubbed up with a little water in a mortar, is placed in a Wolfbauer's flask (a double flask shaped like a figure 8) with 50—80 c.c. of water, 100—150 c.c. of ether, and a drop of phenolphthalein. After vigorous shaking, dilute potash is added until a pink colour is obtained, and the flask is again well shaken. The ethereal layer is filtered and distilled, and the fat, after drying at 100°, is, if necessary, again filtered. In about 45 specimens of genuine cheese, the Reichert-Meissl number ranged from 23·1 to 32·6, only two specimens (a Limburg, and a Swiss green cheese) showing lower numbers (20·1 and 15·4 respectively, with the abnormally low saponification number 216), whilst the four artificial cheeses examined gave only 1·7—3·1.

The best method of estimating the water is to expose 10 grams of the cheese, cut into small pieces, in a vacuum over sulphuric acid at the ordinary temperature for 24—36 hours, and to finish by 2—6 hours at 100°. The loss of volatile acids is by this means reduced to a minimum, and the cheese is left in a porous condition, in which state it is easily pulverised without adding sand, and is very readily extracted with ether. The ether extract rarely contains notable proportions of non-fatty organic matters. The crude fats may be partially purified by redissolving in cold ether, or by shaking the ethereal solution with water or dilute alkali. Light petroleum presents no advantage over ether for the extraction of the fats.

M. J. S.

Glucosides contained in Digitalis Leaves, and their Estimation. By C. C. KELLER (*Chem. Centr.*, 1897, i, 1211; from *Ber. Pharm. Ges.*, 1895, Heft 11).—According to the author, the leaves of digitalis contain the three glucosides, digitoxin, digitonin, and digitalin, which are identical with the glucosides contained in the seeds. To estimate the quantity of digitoxin, the leaves are extracted with 70 per cent. alcohol, the solution evaporated, the residue taken up with water, basic lead acetate added, the lead removed from the filtrate by sodium sulphate, the solution made alkaline with ammonia, and shaken with chloroform. The digitoxin thus extracted is purified by means of a mixture of ether and chloroform (3:7) in light petroleum.

It forms a yellow solution in hydrochloric acid, which, when heated to 100°, becomes green and then yellowish-green. When a solution of digitoxin in glacial acetic acid containing ferric chloride is treated with concentrated sulphuric acid, the zone of demarcation of the two liquids becomes dark, and in a few minutes the acetic acid turns indigo-blue (Keller's test). The red coloration obtained by treating digitoxin with concentrated sulphuric acid is probably due to the presence of traces of digitalin. The above process may be used for the valuation of digitalis.

Digitonin is obtained from the aqueous solution after shaking with chloroform, by expelling the ammonia, acidifying with hydrochloric acid, precipitating with tannin, dissolving the tannates in 50 per cent. alcohol, adding lead oxide, evaporating, extracting the residue with dilute alcohol, filtering, and evaporating the solution to dryness. Digitonin, when submitted to Keller's test, gives a bright red coloration.

Digitalin is obtained from the filtrate from the digitonin tannates as follows. More tannin solution and concentrated sulphuric acid are added, the precipitate dissolved in 70 per cent. alcohol, the solution boiled with lead carbonate, the liquid decanted, evaporated with lead oxide, the residue extracted with alcohol, and the solution evaporated. Digitalin, when tested by Keller's reaction, gives a characteristic red zone.

For pharmaceutical purposes, it is sufficient to determine the content of digitoxin. E. W. W.

Influence of certain Drugs on the Analysis of Urine. By BRUNO BARDACH (*Zeit. anal. Chem.*, 1897, 36, 776—784).—*Influence of Nitrates on the Estimation of total Nitrogen.*—Whether the original method of Kjeldahl or the special modification of Jodlbauer and Förster is employed, not only is the nitrogen of the nitrate missed, but considerably less is found than is present in other forms. This is due to the intermediate formation of nitrous acid, which then decomposes urea with evolution of nitrogen. By reducing the nitrates with aluminium and soda before adding the sulphuric acid, the total nitrogen present may be estimated with great accuracy. For 10 c.c. of urine, 0.3 gram of ignited aluminium foil and 5 c.c. of soda of sp. gr. = 1.34 may be used. The reduction is allowed to proceed for $\frac{3}{4}$ -hour in the cold, and the liquid is then carefully boiled for 5 minutes, and air is aspirated through the flask for $\frac{3}{4}$ -hour longer, the gases being passed through standard acid with precautions against the transport of soda by the hydrogen. The concentrated sulphuric acid (30 c.c.) is then added, and the process finished as described by Kjeldahl. To ensure the complete absorption of the ammonia, it is desirable to pass the hydrogen twice through acid.

Titration of Urea by Liebig's Method.—In presence of iodides, the end-reaction occurs too soon, although this effect can to some extent be compensated by the addition of sodium chloride. Ammonium chloride, on the contrary, delays the end-reaction very seriously.

Estimation of Uric Acid.—Salkowski's method (*Abstr.*, 1872, 333) is not appreciably influenced by piperazine, lysidine, or potassium iodide, in the proportions of the ordinary doses. M. J. S.

Estimation of Alloxuric Bases. By ERNST L. SALKOWSKI (*Pflüger's Archiv.*, 1898, 69, 268—306).—The paper proposes certain modifications of the silver method of estimating uric acid and the alloxuric (xanthine) bases, and criticises Camerer's work on the subject.

W. D. H.

The Krüger-Wulff Method for Estimating Alloxuric Compounds. By ERNST L. SALKOWSKI (*Chem. Centr.*, 1897, i, 1076—1077; from *Deutsch. med. Woch.*, 23, 213—216).—The author thinks that his process, involving the use of silver solution, is preferable to the method based on the action of a cuprous salt; silver throws down the alloxuric bases, all but completely.

L. DE K.

Estimation of Caffeine in Coffee. By ARTHUR FORSTER and RUDOLF RIECHELMAN (*Chem. Centr.*, 1897, i, 1259—1260; from *Zeit. öffentl. Chem.*, 3, 129—131).—Twenty grams of the ground roasted coffee is boiled four times with 200 c.c. of water, and after the joint infusions have been made up to 1 litre and filtered, 600 c.c. of the filtrate is extracted in a specially constructed apparatus for 10 hours with chloroform, the liquid having previously been made alkaline with aqueous soda. The chloroform is distilled off, the residue treated by Kjeldahl's process, and the amount of caffeine calculated.

The liquid also contains another alkaloid, which although it cannot be extracted by an immiscible solvent, may be precipitated by phosphomolybdic acid. This alkaloid may be obtained from the precipitate by treating it with lime and extracting with alcohol; probably it is identical with Paladino's caffearine.

L. DE K.

Estimation of Caffeine in Tea. By C. C. KELLER (*Chem. Centr.*, 1897, i, 1134—1135; from *B. Pharm.*, 7, 105—112).—Six grams of the sample is treated in a separating funnel with 120 grams of chloroform, and after soaking for a few minutes, 6 c.c. of a 10 per cent. solution of ammonia is added, and the whole shaken for half an hour. After leaving it for 3 to 6 hours, 100 grams of the chloroform extract, representing 5 grams of tea, is drawn off, distilled to dryness, and the residue moistened with 3 c.c. of absolute alcohol; this, when evaporated in a strong current of air, causes the chlorophyll to separate mechanically. The caffeine is purified by warming it with a mixture of 7 c.c. of water and 3 c.c. of alcohol; 20 c.c. more water is then added, and the liquid filtered. On evaporation, it leaves pure, weighable caffeine.

The percentage of caffeine in various commercial samples of tea is tabulated.

L. DE K.

Reagents for the Detection of Certain Alkaloids. By ALPHONSE L. BROCIER (*Zeit. anal. Chem.*, 1898, 37, 62; from *Pharm. Zeit. Russ.*, 28, 778).—A solution of 1 gram of potassium perruthenate in 20 c.c. of concentrated sulphuric acid gives the following colorations:—with *solanine*, a gradually developing red colour, which disappears on heating; with *ononine*, an immediate brownish-red; with *chelidonine*, green; with *imperatorine*, blue changing to green. A solution of 1 gram of ammonium uranate in 20 c.c. of sulphuric acid (which must be freshly prepared) gives:—with *codeine*, a blue coloration

on gently warming ; with *imperatorine*, blue disappearing on warming ; with *morphine*, a dirty green on warming ; and with *chelidonine*, a slowly developing green coloration.

M. J. S.

Detection of Opium Alkaloids. By GUSTAVE BRUYLANTS (*Zeit. anal. Chem.*, 1898, 37, 62—63 ; from *Pharm. Zeit. Russ.*, 28, 778).—The following colour reactions are given by the various opium alkaloids with the Fröhde-Buckingham reagent and the modifications of the test suggested by the author (Abstr., 1896, ii, 132).

	Fröhde reagent in the cold.	Fröhde reagent after warming.	Potassium nitrate added to hot mixture.
Morphine	Violet.	Green.	Red, then yellow.
Apomorphine...	Greenish-blue.	<i>Ibid.</i>	<i>Ibid.</i>
Oxymorphine...	Blue.	<i>Ibid.</i>	The violet changes to red.
Codeine	Dirty green, then blue.	<i>Ibid.</i>	Like morphine.
Narceine	Blue changing to green.	Dirty green.	Like morphine.
Narcotine	Green, then greenish-brown.	Green.	Violet, then transient red.
Papaverine	Green, then blue, then red.	Green, then blue, then red.	Green rapidly disappearing.
Meconine ...	Very transient green.	Dirty blue.	<i>Ibid.</i>
Cryptopine	Dirty green, then greenish-brown.	Dark brown.	<i>Ibid.</i>

M. J. S.

Estimation of Morphine in Opium. By CLEMENTE MONTEMARTINI and D. TRASCIATTI (*Gazzetta*, 1897, 27, ii, 302—335).—Most of the test estimations of morphine in opium by various methods have been made on a few samples of opium of approximately the same composition. The authors have determined the morphine in nine samples of opium (A to K), differing widely in composition, by the principal methods, the results being summarised in the accompanying table ; the best were obtained by a method which the authors themselves have elaborated, depending on extracting the morphine with a sodium chloride solution. The analysis is carried out as follows. Ten grams of the powdered opium, dried at 100° is macerated in a mortar with 90—100 c.c. of a 20 per cent. sodium chloride solution for 1 hour, and then thrown on to a small filter, the residue being again treated for 1 hour with 60 c.c. of the sodium chloride solution. The mixture is then filtered, and the residue repeatedly treated with sodium chloride solution until a colourless filtrate is obtained, or until a drop gives no reaction with Fröhde's reagent. The mixed filtrates are evaporated to dryness on the water bath, and the powdered residue is repeatedly extracted with boiling absolute alcohol (300—350 c.c.) until the extract gives no reaction with Fröhde's solution ; the alcoholic solution is evaporated, and the residue, after being covered with 15 c.c. of very dilute ammonia and left for 24 hours, is collected on a tared filter, washed with aqueous morphine solution

until the washings are colourless, and dried at 100°. The filter containing the morphine is then put into a tap funnel and covered with chloroform; the latter is run off and the treatment repeated until, on evaporating a few drops, taking up the residue with hydrochloric

Sample.	Italian Pharma- ceutics of 1892.	Helffenberger.		Langlois.	Guichard.	Cannapin and Van Eijk.	Perger.	Squibb.	With NaCl.
		Aliquot parts.	With exhaustion.						
A.	14.35	11.05	10.46	—	—	10.94	16.84	—	16.70
B.	12.30	11.40	11.52	—	—	11.76	15.60	15.02	15.80
C.	10.10	7.68	10.28	10.09	14.36	10.76	12.29	12.40	12.00
D.	6.40	5.10	4.40	5.89	—	6.74	8.60	10.85	8.36
E.	10.12	10.15	10.44	11.60	11.70	11.42	13.04	13.11	13.55
F.	4.08	—	—	—	—	—	8.77	8.89	8.67
G.	—	—	—	—	—	13.00	—	16.09	16.55
H.	—	—	—	5.53	19.42	5.84	11.37	11.07	11.42
K.	7.36	—	—	9.58	14.24	10.12	12.82	13.58	13.51

acid and adding soda, no turbidity is obtained. The morphine is then again brought on to a tared filter, dried at 100°, and weighed; the whole determination takes about 4 days for its completion.

The most concordant results are obtained by this method and by those of Perger and Squibb. W. J. P.

Detection of Atropine in Corpses. By PAUL SOLTSIEN (*Chem. Centr.*, 1897, 1, 1002; from *Zeit. öffentl. Chem.*, 3, 115—116).—In the case of a child who died through eating atropine pills, this alkaloid could not be detected in the alkaloidal residue obtained from the kidneys, liver, and spleen, either by the physiological test or by Vitali's reaction; neither could any atropine be obtained from the stomach or its contents, or from the duodenum or oesophagus. In the urine, however, a trace of alkaloidal residue was obtained which, although it could not be detected by Vitali's reaction, gave a very good physiological test when applied to the eye. L. DE K.

The Precipitation of Proteids. By N. C. HENRIK SCHJERNING (*Zeit. anal. Chem.*, 1897, 36, 643—663).—A marked difference is produced in the properties of albumin and other proteids by the presence or absence of saline matter, the ash-free proteids evidently possessing, in some respects, the character of acids. The precipitation of the proteids by the four reagents employed by the author (*Abstr.*, 1896, ii, 631), namely, stannous chloride, lead acetate, ferric acetate, and uranium acetate, may therefore be regarded as resulting from the formation of insoluble protein salts of the heavy metal. To investigate the question whether these precipitations would be furthered by the presence of normal salts, containing in the first place a different basic radicle, and in the second case a different acid radicle from that in the precipitant, two series of experiments were made, employing

beer as the proteid solution and working strictly according to the methods laid down in former papers. In the first series, varying amounts of a calcium salt were added before the precipitating reagent, the acid radicle of the calcium salt employed being in each case identical with that of the precipitant. The result was that the amount of nitrogenous matter precipitated by stannous chloride increased with increasing additions of calcium chloride but with the three other reagents the reverse effect was produced. On this account, it is advocated as an improvement in the precipitation of albumin by stannous chloride to add 10 c.c. of a 10 per cent. calcium chloride solution, and to wash the precipitate with a 1 per cent. solution of the same. In the second series, a new acid radicle was introduced (or rather the amount already present was augmented) by the addition of sodium phosphate. Up to a certain point, this caused an increased precipitation of nitrogenous matter by each reagent, but as soon as the added phosphate was sufficient to precipitate the reagent by itself, the amount of nitrogenous matter thrown down diminished.

The addition of phosphate is therefore only desirable in cases where the proteid solution is very deficient in phosphoric acid, and then only to the amount existing in normal beer, namely, about 0.02 gram of P_2O_5 in 25 c.c. These cases may be recognised by the incomplete precipitation of the ferric acetate by the original solution.

The author has now applied the above method of analysis to solutions of egg-albumin, milk, decoction of yeast, Witte's peptone, Liebig's meat peptone, and meat extract, diastase (Merck's) and urine. The results indicate that whereas beer-wort seems to contain only four proteids, milk contains a fifth, which is not precipitable by stannous chloride, but is precipitated by all the other reagents, including magnesium sulphate. This, which the author distinguishes as albumin II, seems to agree in amount with the lactalbumin and lactoglobulin of König, whilst the albumin I precipitable by stannous chloride agrees closely with the amount of casein. Witte's peptone and Liebig's meat peptone contain propeptones (albumoses), but no peptones; Liebig's meat extract shows 11 per cent. of the nitrogen in the form of peptones, whereas König and Bömer found only traces (Abstr., 1896, ii, 83). In normal urine only traces of proteids are discoverable.

M. J. S.

Modification of Oliver's Hæmoglobinometer. By ERNEST SOLLY (*Proc. Physiol. Soc.*, 1897—8, 23).—Instead of using a dark room, a box acting as a portable dark chamber which can be illuminated with a small candle or electric lamp is employed, and modification in the extent of dilution of the blood is also suggested. W. D. H.

General and Physical Chemistry.

Refractivities of Air, Oxygen, Nitrogen, Argon, Hydrogen, and Helium. By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1897, 62, 225—232).—By means of an apparatus similar to that described by Lord Rayleigh (*Abstr.*, 1896, ii, 598), the refractivity of hydrogen was compared with that of air, and subsequently the hydrogen was compared with oxygen and with nitrogen free from argon. Air, oxygen, and nitrogen, were then compared with one another, and with argon. Placing air in each case equal to unity, and calculating the refractivities of the other gases, the following table was obtained.

	Directly Compared.	Through			
		Oxygen.	Nitrogen.	Hydrogen.	Argon.
Hydrogen.....	0·4733	0·4737	0·4727	—	—
Oxygen.....	0·9243	—	0·9247	0·9237	0·9261
Nitrogen	1·0163	1·0155	—	1·0170	1·0191
Argon	0·9596	0·9577	0·9572	—	—
CO ₂	—	1·5316	—	—	—

It has been tacitly assumed that the refractive index for a mixture of gases is that of those of their constituents, taken in the proportion in which they occur. The index of refraction of air, calculated from the above determinations, is about 0·35 per cent. too low, that of a mixture of about equal volumes of hydrogen and helium is 3 per cent. higher than the value found, and a mixture of oxygen and carbonic anhydride has a calculated refractivity that is less than the observed.

The effect of mixing equal volumes of hydrogen and helium, each of which has too large a coefficient of elasticity, is to cause each to occupy twice the volume that they previously occupied, and to halve approximately the pressure for each. The pressure is therefore lower than it would be for an absolutely ideal gas, for each gas, hydrogen and helium. The sum of these pressures will accordingly be too low, or transposing, the sum of the volumes will be too great. The opposite argument holds for air. But if the refractive power is a function of the dielectric constant, and hence of the co-volumes of the gases, it follows that gases are not, as postulated by Dalton, indifferent to one another's presence, but that they modify one another's properties in the same manner as do liquids, although to a different extent. Although at low pressures and large volume, measurements of pressure and volume may not be accurate enough to lead to the detection of this mutual action, the refractivity seems to be a means delicate enough to be used for this purpose.

H. C.

Optical Constant of Sodium. By PAUL DRUDE (*Ann. Phys. Chem.*, 1898, [ii], 64, 159—162).—With light polarised at an angle of 45° to the plane of incidence, an angle of incidence of 65°, and using

sodium light, the author finds for the index of refraction of sodium $n = 0.0045$, and for that of absorption $k = 580$. Sodium has therefore the smallest index of refraction found for any metal. H. C.

Refractive and Dispersive Power of Combined Silicon. By GINO ABATI (*Gazzetta*, 1897, 27, ii, 437—455).—The author has determined the refraction constants of a number of silicon compounds for the rays H_α , H_β , H_γ , and D; the chief results for the ray H_α are summarised in the accompanying table. The substances were examined

Compound.	t .	d at t° .	$P \frac{\mu_{H_\alpha} - 1}{d}$	$P \frac{\mu_{H_\alpha}^2 - 1}{d \mu_{H_\alpha}^2 + 2}$	Atomic refraction of silicon for	
					μ .	μ^2 .
SiCl_4	22.9°	1.47556	47.26	28.55	8.06	4.47
SiBr_4	23.5	2.77222	70.07	40.48	8.87	4.68
SiEt_4	22.3	0.76819	79.62	47.91	13.62	7.27
SiEt_4	22.7	0.76890	79.38	47.77	13.38	7.13
Si(OMe)_4	22.0	1.02804	54.11	33.09	7.31	4.37
Si(OEt)_4	20.0	0.9320	84.84	50.52	7.64	3.56
Si(OPr)_4	22.7	0.9158	115.18	69.81	7.58	4.61
$\text{Si}_2\text{O(OPr)}_6$	22.6	0.97694	176.88	107.02	6.04	3.82
Si(OH)_4	24.1	—	26.44	16.21	10.04	5.73
Quartz	0	2.65085	12.36	7.16	6.76	4.00
Tridymite	15	2.304	12.39	7.34	6.79	4.18
Opal	15	2.15	11.56	—	5.96	—

in the pure state with the exception of colloidal silicic acid, which was examined in a 2.153 per cent. aqueous solution. The atomic refraction of silicon calculated by either the μ or μ^2 formula varies considerably in the different compounds. W. J. P.

Refractive Indices of the Blue and Green Solutions of the Chrome Alums. By CHARLES SORET, ARN. BOREL, and EUG. DUMONT (*Chem. Centr.*, 1897, i, 1088; from *Arch. Sci. phys. Genève*, [iv], 3, 376—381).—Observations were taken with 4 to 6 per cent. solutions of potassium and ammonium chrome alum for the rays C, D, and F. The mean refractive index of the blue solutions is greater than that of the green solutions by 47 units of the fifth decimal. The difference is the same for solutions of both the alums. The observations were made at about 20°. H. C.

Refraction of Metallo-carbonyls. By RAFFAELE NASINI (*Gazzetta*, 1897, 27, ii, 556—559).—The author objects to Ferreira da Silva's statement (*Abstr.*, 1897, ii, 406) of the views of Mond and Nasini, respecting the metallo-carbonyls. W. J. P.

Optical Activity. By L. TORÚGAEFF (*Ber.*, 1898, 31, 360—368).—The author considers that for comparisons of the optical activities of different substances, it is better to use the molecular rotation, $[M]_D = M \times [\alpha]_D$, and not the usual constant, the specific rotatory power $= [\alpha]_D$.

The following numbers have been obtained for the different menthylic salts of normal acids.

	$[\alpha]_D$.	$[M]_D$.	d 20°/4°.	B. P. at 15 mm.
Menthol:	-50.0°	-78.0		
Menthylic formate.....	-79.52	-146.3	0.9359	98°
„ acetate	-79.42	-157.3	0.9185	108
„ propionate	-75.51	-160.2	0.9184	118
„ butyrate	-69.52	-156.9	0.9114	129
„ valerate	-65.55	-157.3	0.9074	141
„ hexoate.....	-62.07	-157.7	0.9033	153
„ heptoate	-58.85	-157.7	0.9006	165
„ octoate	-55.25	-155.8	0.8977	175

The salts were obtained by the action of the various acid chlorides, in slight excess, on menthol; the products were washed with sodium hydroxide, dissolved in ether, dried with potassium carbonate, and, after distilling off the ether, carefully fractionated under diminished pressure. The portions taken for the optical constants boiled within a few tenths of a degree. The measurements were made in a Laurent half shadow polarimeter at a temperature of 20—20.5°. The tube used was 100 mm. long. The most important generalisation which can be drawn is, that whilst the function $[\alpha]_D$ is at a maximum with the formate and then gradually gets smaller, the function $[M]_D$ reaches its maximum with the acetate, and then remains practically constant.

A similar result is obtained when the specific rotatory powers of the salts of *l*-amylic alcohol given by Guye and Chavanne (Abstr., 1895, i, 202, 317) are converted into the corresponding molecular rotations. A maximum is reached at amylic propionate, and the higher members of the series have roughly the same molecular rotation, namely, -4.33°.

Similar results may be obtained for other homologous series, namely, alkylic salts of optically active valeric acid (Guye and Chavanne, Abstr., 1893, ii, 561), the derivatives of *l*-menthylamine (Binz, *Inaug. Diss.*, 1893), the ethereal salts of glyceric and of diacetylglyceric acid, Frankland (Trans., 1893, 511, 1410; 1894, 750), and also the alkylic salts of tartaric acid (Pictet and Freundler).

In the different series, the maximum is reached at very different points; in some cases near the beginning of the series, in others towards the end. In certain series, the maximum appears to lie beyond any members of the series hitherto investigated. In series in which a change in the sign of the rotation occurs, it seems probable that no maximum and no constant molecular rotation will be found.

J. J. S.

Fluorescence and Chemical Constitution. By RICHARD E. MEYER (*Ber.*, 1898, 31, 510—514).—The author has endeavoured to bring into line the numerous facts relating to fluorescence, and has traced the phenomenon to the presence of certain groups which he designates as fluorophores (this vol., ii, 105). The applicability

of these generalisations has been called in question by Pawlewski (this vol., i, 322), to whom the present paper constitutes a reply.

The author describes a simple form of apparatus which has been found useful in the demonstration of fluorescence phenomena.

M. O. F.

Variation of the Electromotive Force of Different Forms of the Clark Standard Cell with Temperature and with Strength of Solution. By HUGH L. CALLENDAR and H. T. BARNES (*Proc. Roy. Soc.*, 1897, 62, 117—152).—The authors describe a lengthy series of experiments carried out with different forms of the Clark standard cell. A modification has been adopted, which is termed the Board of Trade "crystal" cell, in which the cell above the mercurous paste is filled with moist crystals, instead of with saturated solution. These cells have no appreciable diffusion-lag, and are not surpassed in quickness by any other form. Over the range 0° to 28° , we may take the formula $E_t = E_{15} - 0.001200(t - 15) - 0.0000062(t - 15)^2$, as representing the temperature variation of the E. M. F. of these cells within about one-twentieth of a millivolt between these limits. Several forms of hermetically sealed cells are described of a W or an inverted Y pattern. Determinations have been made of the densities of zinc sulphate solutions and of the solubility of zinc sulphate at different temperatures. At about 38.8° , a break in the solubility curve, and a change in the continuity of the curve representing the temperature variation of the E. M. F. were observed, and referred to the change of the hydrate $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ to the hydrate $\text{ZnSO}_4 + 6\text{H}_2\text{O}$ (compare Jaeger, this vol., ii, 202).

H. C.

A New Kind of Transition Cell. By ERNST COHEN (*Zeit. physikal. Chem.*, 1898, 25, 300—304).—The author described (Abstr., 1894, ii, 340) an electrical cell in which an E. M. F. is produced by means of electrodes placed in saturated solutions of the two forms of a compound capable of undergoing a transition change, and an element where the temperature coefficient changes abruptly at the transition temperature (Abstr., 1894, ii, 407). Another class of cell is of the following type. Electrode reversible with respect to the anion | saturated solution in presence of stable solid phase | electrode reversible with respect to the cation. Such a cell is the Clark cell, consisting of mercury in mercuric sulphate, | saturated solution of zinc sulphate, | zinc, and in this cell the temperature coefficient should change abruptly at the temperature of transition from $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ to $\text{ZnSO}_4 + 6\text{H}_2\text{O}$. Callendar and Barnes (preceding abstract) found this temperature to be 38.75° ; solubility experiments gave the value 39.3° , and by the dilatometric value the temperature 38.5° was obtained.

L. M. J.

Action of Drop-electrodes. By WILHELM PALMAER (*Zeit. physikal. Chem.*, 1898, 25, 265—283).—During the formation of the drop in a mercury-dropping electrode the surface of separation of mercury and calomel solution is increased, and hence, if the solution tension of the mercury is less than the pressure of the mercury ions, the latter pass into the drop, whilst the equivalent quantity of chlorine ions form the double layer at the surface until the normal potential difference is

reached. When this drop reaches the lower surface of mercury, already in its normal state, the mercury and chlorine ions again pass into solution reforming calomel, so that it follows that the concentration of the calomel decreases above and increases below. By independent mercury electrodes in the electrolyte at the upper and lower portions, and a mercury electrode in an independent calomel solution, the concentration was found to change in the manner expected. The potential difference soon attains a constant value, and, if the dropping be then stopped, the E. M. F. falls, slowly if undisturbed, but immediately if the liquid be stirred. Owing to the formation of a mercury emulsion in the liquid, the liquid does not reach a normal state, even by remaining 24 hours without stirring. The effect of change of level of the electrode, diameter of dropping-tube, and head of mercury were investigated, and the concentration of the mercury ions in the neighbourhood of the dropping-tube was found to be about one-tenth that of a saturated calomel solution, that is, about 1.1×10^{-7} normal.

L. M. J.

Electric Conductivity of Nitric Acid. By VICTOR H. VELEY and J. J. MANLEY (*Proc. Roy. Soc.*, 1897, 62, 223—225).—Determinations were made of the electric conductivity of nitric acid of percentage concentrations varying from 1.3 to 99.97, purified, as far as possible, from the reduction products of the acid and other impurities. A considerable quantity of the practically anhydrous, 99.97 per cent., acid was prepared, and some of the properties of this examined. It has no action on (i) copper, (ii) silver, (iii) cadmium, or (iv) mercury, all of high degree of purity, or (v) commercial magnesium, at ordinary temperatures; purified iron and commercial granulated tin were not affected by the acid, even when boiling. Purified zinc was slightly acted on, but sodium immediately caught fire. The acid has no action whatever on calcium carbonate at ordinary temperatures or the boiling point. Flowers of sulphur and iron pyrites dissolve quickly in the gently-warmed acid. The following results were obtained for the density of the 99.97 per cent. acid, corrected for weighing in a vacuum. Density, $4^{\circ}/4^{\circ} = 1.54212$; $14.2^{\circ}/4^{\circ} = 1.52234$; $24.2^{\circ}/4^{\circ} = 1.50394$.

The specific resistance decreases for percentage concentrations from 1.30 to 30, at first more, then less rapidly; from this point the resistance increases slowly up to 76 per cent., thence more rapidly until a maximum is reached at 96.12 per cent., when a sudden reversal takes place. There is a positive temperature coefficient of conductivity for percentage concentrations from 1.3 to 96.12, but from this point up to 99.97 per cent., the acid has a negative coefficient. As nitric acid of 96—99.97 per cent. would contain few, if any, free ions, this result is opposed to the theory of ionic dissociation. On the other hand, points of discontinuity are shown on the conductivity curve corresponding approximately with the composition required for the hydrates $\text{HNO}_3 + 2\text{H}_2\text{O}$, $\text{HNO}_3 + \text{H}_2\text{O}$, $2\text{HNO}_3 + \text{H}_2\text{O}$, and $\text{HNO}_3 + 10\text{H}_2\text{O}$.
H. C.

Energy of some Toluenesulphonic and Xylenesulphonic Acids. By P. BONOMI DA MONTE and A. Zoso (*Gazzetta*, 1897, 27, ii, 467—475).—The authors have examined toluene-*o*-sulphonic acid,

$C_6H_5 \cdot CH_2 \cdot SO_3H$, paraxylene-*o*-sulphonic acid, $C_6H_4Me \cdot CH_2 \cdot SO_3H$, tolueneparasulphonic acid, $C_6H_4Me \cdot SO_3H$, and paraxylenesulphonic acid, $C_6H_3Me_2 \cdot SO_3H$, determining the electrical conductivity of their aqueous solutions, the speed with which they invert cane-sugar, and their cryoscopic behaviour. All four acids are nearly wholly electrolytically dissociated in aqueous solutions of moderate dilution, and have about the same affinity constant as hydrochloric acid. The values of μ_∞ for the four acids in the order named above are 350.98, 350.01, 350.49, and 350.38, the corresponding values for the sodium salts being 75.18, 74.21, 74.69, and 74.58 respectively. The differences observed between the acids are so small that no influence can be at present assigned to the position of the methyl groups. W. J. P.

Energy of some Bases of Mixed Function. By GIACOMO CARRARA and U. ROSSI (*Gazzetta*, 1897, 27, ii, 505–532).—The authors have determined the electrical conductivities of a number of betaine and thetine compounds, the experimental data being summarised in the accompanying table.

Substance.	μ_{1024} .	μ_∞ .	Mean value of K_3/K_4 .
Betaine hydrochloride	111	—	78.7
„ hydrobromide	114	115.8	100.2
Dimethylthetine hydrochloride ..	115	116.9	38.1
„ hydrobromide ..	—	119.7	26.5
Diethylthetine hydrochloride	103	105.2	50.0
„ hydrobromide	106	107.8	40.3
Dimethyl- α -propionylthetine hydrochloride...	103	105.2	36.4
„ „ hydrobromide ..	105	108	34.4
„ - β - „ hydrobromide...	105	108	2248
Diethylselenetine hydrobromide	105	108	27030
Ethylie dimethylthetine bromide	103.93	108	—
Triethylsulphine chloride.....	102.2	105.8	—

The electrical conductivities of the hydrochlorides and hydrobromides of betaine, dimethyl- and diethyl-thetine, and dimethyl- α -propionylthetine are of the same order of magnitude as those of hydrogen chloride and bromide, especially in dilute solutions; the behaviour of diethylselenetine, dimethyl- α -propionylthetine, and the ether of dimethylthetine is different, these substances undergoing much less hydrolysis.

Substance.	AC .	K .
Hydrogen chloride or bromide	0.000286	—
Dimethylthetine hydrobromide.....	0.000152	0.00571
„ hydrochloride.....	0.000157	0.00523
Betaine hydrochloride	0.000103	0.0172
„ hydrobromide	0.000101	0.0181
Dimethyl- α -propionylthetine hydrochloride	0.000150	0.00604
„ hydrobromide	0.000027	0.355

The authors have also determined the affinity constants of the various bases by Walker's method, which consists in heating a solution of the hydrochloride or hydrobromide of the base with methylic acetate at 25—26°, withdrawing samples from time to time, and titrating against standard potash; x is the quantity of methylic acetate hydrolysed in t minutes, A the quantity originally present and the reaction is a monomolecular one obeying the equation $\log \frac{A}{A-x} = \frac{AC}{t}$. If K_a be ten times the affinity constant obtained with hydrogen chloride or bromide, K_1S ten times the affinity constant obtained with the hydrolysed salt, and K the affinity constant of the base, then $K = (K_a - K_1S)/K_1S$. The accompanying table gives the values of AC and K obtained. Comparison of the figures given with those obtained by Walker shows that the betaine and thetine bases are more powerful than thiocarbimide, carbimide, or acetamide, and less powerful than asparagine or glycocine.

W. J. P.

Dielectric Constants of certain Organic Substances at and below the Temperature of Liquid Air. By JAMES DEWAR and JOHN A. FLEMING (*Proc. Roy. Soc.*, 1897, 61, 358—367. Compare this vol., ii, 9).—The authors have examined formic acid, methylic alcohol, amylic alcohol, quinoline, tetrethylammonium hydroxide, and phenol, and find that these substances have in the liquid or solid condition, and at temperatures above -100° , high or very high dielectric values, but all have their dielectric constants reduced to a value not far from 2.5 when they are cooled to the temperature of liquid air. The dielectric constants of castor oil and olive oil are reduced in value when these oils are cooled to -185° . Carbon bisulphide, ether, ethylic nitrate, a solution of sulphur in carbon bisulphide, and a 10 per cent. solution of metallic sodium in absolute alcohol all undergo a reduction in the value of the dielectric power, large or small, which these substances possess at normal temperatures. The presence of the radicles hydroxyl, carbonyl, and carboxyl, always produces relatively high dielectric values in the substances containing them, when these are in the liquid state, and at temperatures not very far below their freezing points. When these substances are, however, frozen and cooled to the temperature of liquid air, all of them suffer a reduction in dielectric power, and their dielectric constants are reduced to values not far from 2.5 at the temperature -185° or a little below. The action of the low temperature is thus to annul the effect of the radicle. No exception has so far been found to the rule that pure organic substances have a dielectric constant of from two to three times that of vacuous space when they are cooled to the temperature of boiling liquid air, no matter what value their constant may have when in the liquid condition.

H. C.

Dielectric Constants of Metallic Oxides dissolved or suspended in Ice Cooled to the Temperature of Liquid Air. By JAMES DEWAR and JOHN A. FLEMING (*Proc. Roy. Soc.*, 1897, 61, 368—379).—The presence of caesium hydroxide, lithium hydroxide, bismuth oxide, aluminium oxide, finely divided sulphur, or finely divided gold in ice was found to make little or no difference in its

dielectric power when cooled to the temperature of liquid air. The presence, to about the same extent, of the hydroxides of potassium, sodium, rubidium, or the oxides of copper, iron, or lead, causes a very great increase in the dielectric power of the ice at that low temperature. The dielectric curves are, however, all seen to be tending downwards in such a way as to show that at still lower temperatures it is probable the effect of the oxides or hydroxides would be annulled and the dielectric constants of all be reduced to a value not far from that of pure ice. The exception to this tendency, so far as yet observed, appears to be in the case of the oxide of copper, which, when suspended in ice, causes it to possess the remarkably high dielectric value of 150 even at the temperature of liquid air. It is possible, however, that in this case the conductivity of the yet insulated particles of oxide may account for the result. The effect of the solvent is also exceedingly marked. Oxide of copper suspended in ice has a dielectric value of about 150 at -185° , oxide of lead suspended in ice has a value of about 80 at the same temperature. If, however, the oxide of copper is dissolved in ammonia and frozen, the dielectric constant of this at -185° falls to 2.2, whereas if the oxide of lead is dissolved in 5 per cent. solution of potassium hydroxide and frozen, the dielectric constant rises to 170 at the temperature of liquid air.

The only general conclusion that can as yet be drawn is that the presence of certain oxides or hydroxides of metals in ice, even to the extent of not many per cent., has an immense influence in raising the dielectric power of the ice when taken at the temperature of liquid air, whereas the presence of other oxides or hydroxides chemically analogous has hardly any influence at all.

H. C.

Dielectric Constants of Frozen Electrolytes at and above the Temperature of Liquid Air. By JOHN A. FLEMING and JAMES DEWAR (*Proc. Roy. Soc.*, 1897, 61, 380—396. Compare this vol., ii, 8).—As regards the value of the dielectric constants of frozen electrolytes at the temperature of liquid air, the salts examined may be divided into three broad classes.

I. Those which, when added to water in percentages from 5 to 50, do not much affect the dielectric constant of the water when it is frozen, and, at the temperature of liquid air, have dielectric constants not far from 2.5, or lying between 2 and 3. Such salts are sodium hydrogen carbonate and sulphate, potassium hydrogen carbonate and sulphide, potassium dichromate and iodide, sodium chloride and nitrite, barium chloride and cupric carbonate. These include the acid salts and halogen salts.

II. Those salts which, when added to water in percentages from 5 to 50, raise the dielectric constant of the water somewhat, and yield frozen electrolytes having, at the temperature of liquid air, dielectric constants lying between 3 and 10, that of pure ice at the same temperature being 2.5. Such salts are potassium chromate, sodium sulphate, chlorate and acetate, cadmium borotungstate, potassium aluminium sulphate, plumbic nitrate. These are all highly oxygenated salts.

III. Salts which, when added to water in percentages from 5 to 50,

yield electrolytes which, if frozen, have immensely greater dielectric constants than pure ice at the temperature of liquid air, namely, values from 30 to 70. Such salts are sodium carbonate, borate (borax), thiosulphate and silicate, disodium hydrogen phosphate, and potassium ferrocyanide.

Acid salts were always found to have lower dielectric constants than the corresponding normal salts at the temperature of liquid air. From the downward tendency of the dielectric curves, it would seem probable that, with few exceptions, all frozen electrolytes would, if reduced to temperatures not far above the absolute zero, have their dielectric constants approximately equal, and reduce to a value not far from 2 or 3. At the same time, the electric resistivity of such frozen electrolytes would tend to become infinite, as the temperature is continuously reduced.

H. C.

Dielectric Constants of Organic Substances and Electrolytes at very Low Temperatures. By JAMES DEWAR and JOHN A. FLEMING (*Proc. Roy. Soc.*, 1897, **62**, 250—266).—Several of the authors' previous determinations (this vol., ii, 8 and 9) have been repeated, using Nernst's method for the measurement of dielectric constants, and a frequency of alternation of about 350 in place of 120. For organic substances such as ethylic alcohol, amylic alcohol, ethylic ether, and glycerol, practically the same dielectric values were obtained at the low temperature as in the previous set of observations. On the other hand, for certain other substances such as frozen dilute hydroxides of potassium and rubidium and oxide of copper suspended in ice, the dielectric value at the low temperatures is much diminished by increasing the frequency. Abegg has suggested that the high dielectric values at low temperatures are due to polarisation of the electrodes of the condenser, but the authors show that this can hardly be the case. The dielectric constant may be considered as a function of the frequency and the temperature, and represented therefore by a dielectric surface, which surface has for some substances a region of abnormal dielectric ordinate. Lowering the temperature sufficiently acts in the same manner in reducing the dielectric constant as sufficiently increasing the frequency, and both actions reduce the abnormally large dielectric values of some substances to values more approximately equal to the square of the optical refractive index of the substance.

H. C.

Decomposition of Compounds by Electrical Oscillations. By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1898, **25**, 284—299).—Various organic compounds were exposed in the gaseous state, at low pressure, to the influence of electrical oscillations and the decomposition products were examined. From methylic and ethylic alcohols, mixtures of carbonic oxide, carbonic anhydride, hydrogen, and methane or ethane are obtained, and as the quantity of oxides of carbon is diminished if the decomposition occurs in the presence of phosphorus, the author considers these compounds to be due to secondary actions, the primary reaction being represented by $\text{CH}_3\cdot\text{OH} = \text{CH}_4 + \text{O}$; analogous decompositions occur in the cases of propylic, isopropylic, and allylic alcohols. With acetone and propaldehyde, however, the presence of phosphorus causes no diminution in the

quantity of oxides of carbon ; these are hence produced in the primary decomposition, which is in each case $C_3H_6O = C_2H_6 + CO$. Acetaldehyde undergoes an analogous decomposition, but acetic and propionic acids decompose with the formation of oxygen and the unsaturated hydrocarbon. Methylic acetate and ethylic formate give the same decomposition products, and the chemical formula gives no indication, in the author's opinion, of where the strongest mechanical attraction occurs. A few liquids were also exposed to the oscillatory discharge, and glycerol, glycol, glyoxal, glyceric acid, and oxalic acid were all found to be partially decomposed. Phenol and benzoic acid yielded oxides of carbon and hydrogen, and resinous compounds, the latter, together with hydrogen and acetylene, also being formed from benzene.

L. M. J.

Absolute Temperature. By K. SCHREBER (*Ann. phys. Chem.*, 1898, [ii], 64, 163—185).—A scale of temperature is suggested on which the difference of temperature between two substances *A* and *B*, of which *A* has the higher temperature, shall be 1° , no matter on what portion of the scale this difference falls, when with the reversible transference of 1 unit of heat from *A* to *B*, a transformation of one heat unit into work is connected. In a mathematical treatment of the subject, the author discusses the theoretical and practical advantages of this method of defining temperature.

H. C.

Thermal Conductivity of Nitric Peroxide. By GAETANO MAGNANINI and GIOVANNI MALAGNINI (*Gazzetta*, 1897, 27, ii, 493—497).—The authors have determined, with the aid of a specially designed apparatus, the rate at which gases take up heat when the containing vessel is immersed in a bath at a higher temperature. Air, carbonic anhydride, oxygen, and hydrogen follow Newton's law, the expression $\frac{1}{t} \log \frac{d_1 - d_0}{d - d_0}$ being constant ; d_1 is the temperature of the high temperature bath, d_0 the temperature in the vessel containing the gas after the first minute of heating, and d the temperature of the gas at the time t . Hydrogen has a higher thermal conductivity than air, carbonic anhydride, or oxygen ; at low temperatures, nitric peroxide conducts better than hydrogen, at 70 — 100° worse than hydrogen but better than air, and at 150 — 190° air conducts better than nitric peroxide. The explanation of this is found in the thermal equation $2NO_2 = N_2O_4 + 129k$, the conductivity being increased by molecules of N_2O_4 dissociated into $2NO_2$ by the hot walls of the containing vessel, travelling into the cooler mass of gas, and giving up their heat of dissociation during the act of association. At high temperatures, when the gas is completely dissociated, it conducts less rapidly than air.

The absolute coefficient of thermal conductivity k , at high temperatures, referred to millimetres, milligrams, seconds, and centigrade degrees, can be calculated from the data now given, and Winkelmann's values for air and hydrogen as $k_{150} = 0.0033$.

W. J. P.

Boiling Points of Salts in Ethereal Solution. By ROBERT LESPIEAU (*Compt. rend.*, 1897, 125, 1094—1096).—The boiling points of various ethereal solutions of salts were determined by Raoult's

method, and the general result is to show that the molecular weight of a salt dissolved in ether cannot be determined by a single observation of the boiling point of the solution, since the values vary rapidly with the concentration. It is necessary to determine the limit towards which the values tend when the concentration is continually reduced. This limit has been calculated on the assumption that the curves obtained by taking the increase in the boiling point for abscissæ, and the ratios of this increase to the weight of salt dissolved for ordinates, are right lines. With mercuric chloride, the limit was found to be 272, and with ferric chloride, 153; zinc chloride, 138; antimony chloride, 228; uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 + 6\text{H}_2\text{O}$, 1044. In the latter case, it is clear that the water does not separate from the uranyl nitrate. It has been pointed out that the molecular weights obtained by Raoult's method may be multiples of the true molecular weight, but it does not seem to be sufficiently recognised that if a substance of molecular weight M combines with the solvent S , forming a compound of the formula $MxSy$, Raoult's method at the limit will give, not the number M , but the number xM , in which x may be either less or greater than unity. If x is taken as 2 in the case of uranyl nitrate, and as 0.5 in the case of ferric chloride, the old molecular weights would be obtained. The case of ferric chloride would seem to be settled by other evidence, but the point to which the author calls attention is, he considers, of especial importance in the cases of the solutions of metals in mercury.

C. H. B.

New Process for Determining the Molecular Weight by the Boiling Point Method. By WILLY LANDSBERGER (*Ber.*, 1898, 31, 458—473).—The liquid or solution of which the boiling point is to be determined is placed in a test-tube, the side of which is perforated near the top and the mouth closed by a stopper through which pass a thermometer and a conducting tube reaching to the bottom; this vessel is then fastened by means of a cork into a larger test-tube provided with a side tube which can be connected with a condenser. The liquid is heated by the vapour of the solvent, which is passed in through the conducting tube from a flask or small copper boiler heated by a small flame or water bath. In this way, a constant temperature is reached in 2 to 4 minutes after the commencement of the experiment, so that the determination can be very rapidly carried out. The boiling point of the pure solvent is first determined, and then the inner test-tube is emptied, the required amount of the substance weighed into it, some of the solvent added, and the vapour again passed in. The temperature is observed every one-eighth of a minute, and is taken as constant as soon as three consecutive readings agree. The apparatus is then immediately disconnected from the boiler and condenser, and the inner tube cooled, cleaned externally, and weighed, the empty tube being afterwards weighed, and the weight of the solvent then ascertained by subtraction. A complete determination can be carried out in 25 minutes, and this great saving in time and the simplicity of the apparatus constitute the most important advantages of this method over that of Beckmann. The thermometer used was graduated into

0.05°, and the results obtained agree well with those of other investigators. A. H.

Laws concerning the Molecular Volumes of Liquids. By RAFFAELE NASINI (*Gazzetta*, 1897, 27, ii, 533—555).—The author criticises at length I. Traube's work on the molecular volumes of liquids, and considers that the method of calculation employed by the latter consists only in a method of calculating molecular volumes somewhat different from those previously used. Traube's method is not as accurate as ordinary methods of calculating, owing to the hypotheses which have to be devised and to the uncertainty of the magnitudes of the fundamental values involved. W. J. P.

Determination of the Molecular Weight of Solid Substances. By ANDREAS FOCK (*Ber.*, 1898, 31, 506—508).—A reply to I. Traube (this vol., ii, 213). Traube is not justified in extending his method of molecular weight determination from liquid and dissolved substances to solids, and in stating that "the diminution of the co-volume when a liquid solidifies is only comprehensible on the assumption that the molecules associate." The passage from the liquid to the solid state is only continuous in the case of amorphous solids; in the case of crystalline solids, it is discontinuous, and may well be accompanied by a change of volume, apart from any association of the molecules. Moreover, the author is of opinion that Traube's method cannot be applied legitimately even to liquids. C. F. B.

Viscosity of Hydrogen as affected by Moisture. By Lord RAYLEIGH (*Proc. Roy. Soc.*, 1897, 62, 112—116).—As Crookes states that the viscosity of hydrogen is greatly affected by moisture, experiments were carried out by the author to ascertain whether viscosity might serve as a test of purity. A comparison was made between hydrogen as it issued from the generator without any desiccation whatever, and hydrogen carefully dried by passage through a long tube packed with phosphoric anhydride, but the difference proved to be comparatively trifling. The evidence from the experiments tends to show that residual moisture is without appreciable influence on the viscosity of hydrogen. H. C.

Dissociation of Dibasic Organic Acids. II. By W. A. SMITH (*Zeit. physikal. Chem.*, 1898, 25, 193—264. Compare this vol., ii, 155).—The dissociation constant of the acid and the hydrogen dissociation of the acid sodium salt were determined in the case of a large number of dibasic organic acids. In the case of the oxalic acid series (oxalic to sebacic acids), Noyes' law is well illustrated, namely, the dissociation constant of a dibasic acid is greater, and that of the acid salt is less, the nearer together are the two carboxyl groups. In the higher acids of this series, however, the removal further apart of the acid groups has but little effect on the dissociation of the second hydrogen and these values become constant. In the substituted malonic acids, the effect of substitution is not so clear, but if only analogous acids are compared, it is seen that the dissociation of the second hydrogen decreases when that of the first hydrogen increases;

the reverse holds for the phthalic acids, whilst in the camphoric acids also the dissociation of each hydrogen is similarly affected. The effect of all substituents except hydroxyl is to cause a decrease of the dissociation of the second hydrogen; hydroxyl causes an increase, but the effect on the dissociation of the first hydrogen differs with different acids, so that Noyes' law that both hydrogens are similarly affected is not correct. The numerical results of the determinations are given in the following table, the dissociation of the first hydrogen being given by K_1 , that of the second by K_2 .

Acid.	$10^6 \times K_1$	$10^6 \times K_2$	Acid.	$10^6 \times K_1$	$10^6 \times K_2$
Malonic	1580.0	1.0	Mal. $\alpha\alpha$ -Dimethyl-		
Succinic	66.5	2.3	glutaric	52.0	1.6
Glutaric	47.3	2.7	Fum. $\alpha\alpha$ -Dimethyladipic	42.0	1.7
Adipic	37.6	2.4	Mal. $\alpha\alpha$ -Dimethyladipic	42.0	1.7
Norm. pimelic	32.3	2.6	Methylphenylitaconic ...	236.0	0.62
Suberic	29.9	2.5	Itaconic	151.0	2.3
Azelaic	25.3	2.7	Methylethylitaconic ...	150.0	0.46
Sebacic	23.8	2.6	Dimethylitaconic	140.0	0.46
$\alpha\alpha$ -Trimethylenedicarb-			Fumaric	930.0	18.0
oxylic	21400.0	0.12	Maleic	11700.0	0.39
Dipropylmalonic	11200.0	0.05	Mesaconic	790.0	6.8
Diethylmalonic	7400.0	0.18	Citraconic	3400.0	0.24
Methylbenzylmalonic ...	2660.0	0.12	Phthalic	1210.0	1.7
β -Benzoylisosuccinic.....	2500.0	0.47	$\Delta^{2,6}$ -Dihydrophthalic ...	165.0	1.2
Methylethylmalonic.....	1610.0	0.17	Δ^2 -Tetrahydrophthalic..	76.0	0.32
Benzylmalonic	1510.0	0.49	Hydroxyterephthalic ...	2500.0	21.0
Ethylmalonic	1270.0	0.54	Δ^1 -Tetrahydrotere-		
Isopropylmalonic	1270.0	0.35	phthalic.....	50.0	2.8
Heptylmalonic	1020.0	0.61	<i>trans</i> -Hexahydrotere-		
Octylmalonic	950.0	0.65	phthalic	45.6	2.5
Methylmalonic	860.0	0.76	<i>cis</i> -Hexahydrotere-		
$\alpha\alpha$ -Tetramethylenedi-			phthalic.....	29.7	3.0
carboxylic	800.0	0.30	$\beta\gamma$ -Hydromuconic	102.0	5.3
Dimethylmalonic	760.0	0.31	$\alpha\beta$ -Hydromuconic	175.0	7.9
Tartaric	970.0	59.0	Acetylenedicarboxylic...	very	strong
Malic	399.0	8.3	β -Hydroxycamphoronic.	6500.0	8.4
para-Ethylallylsuccinic ..	269.0	2.3	α -Hydroxycamphoronic.	3200.0	6.5
Fum. Dimethylsuccinic	191.0	1.3	Camphoronic	175.0	8.3
Mal. Dimethylsuccinic...	123.0	0.53	<i>i</i> -Camphoric	22.9	0.72
$\alpha\beta$ -Pentamethylenedi-			<i>d</i> -Camphoric	22.9	0.72
carboxylic	113.0	0.37	<i>l</i> -Camphoric	22.9	0.70
Propylsuccinic	88.6	1.2	Mesocamphoric.....	18.7	0.66
Isuccinic.....	85.0	1.3	<i>l</i> -Isocamphoric	17.4	0.59
Methylsuccinic	86.0	1.6	Citric, 1st H.....	820.0	
Fum. $\alpha\alpha$ -Dimethyl-			„ 2nd H		32.0
glutaric	58.0	1.5	„ 3rd H.....		0.70

L. M. J.

Equilibrium in Systems of Three Components, where Two Liquid Phases may exist. By FRANS A.H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1898, 25, 305—331).—In a previous paper (Abstr., 1897, ii, 483), the author considered the general case of equilibrium in the above system when only one solid phase exists, and this one of the components, and he now extends the theoretical investigation to the

case where two solid phases, both components, may be present. The various forms of equilibrium curves possible, and their physical interpretation, are fully considered with the aid of the usual equilateral diagrams. In many cases, labile portions of the curve are indicated, and hence certain transition temperatures occur; for example, where a solid phase *A*, in liquid *B*, forms two liquids, one containing a high, the other a low percentage of the component *A*. The effect of the addition of a third component on this transition temperature is investigated. Two cases occur, where the component added is more soluble in (1) the liquid with low percentage of *A*, (2) the liquid with high percentage of *A*. In the first case, the transition temperature is raised, an example occurring in the case of the equilibrium of ethylenic cyanide, water, and sodium chloride, the transition temperature of the first two components being raised by the addition of the third. In the second case, the transition temperature is lowered, as, for example, by the addition of ether to the system, ethylenic cyanide and water. This two-fold influence of foreign compounds may frequently be of considerable importance in purification by crystallisation. The two cases are also considered from the thermodynamical standpoint and the results obtained above, experimentally and from the diagrams, are so deduced.

L. M. J.

Coloration of the Ions. By GIACOMO CARRARA and A. MINOZZI (*Gazzetta*, 1897, 27, ii, 455—467).—The authors have examined solutions of anhydrous copper sulphate in dry methylic alcohol, and find that the absorption spectra, as recorded photographically, are the same for aqueous and methylic alcohol solutions of the same concentration. A quantitative examination of the absorption spectra shows that the absorption for the wave-lengths $\lambda = 668$ — 650 , 640 — 622.5 , and 586 — 573.7 , in concentrated solutions, is stronger for aqueous than for methylic alcohol solutions, whilst for dilute solutions the converse is true. Of the curves obtained by plotting concentration against absorption, those for aqueous and methylic alcohol solutions cross each other, but the points at which they cut are different for the different wave-lengths.

Determinations of the electrical conductivity of methylic alcohol solutions of copper sulphate show that, at ordinary temperatures, more dissociation always exists in the alcoholic than in the aqueous solutions of the same concentration. No simple relation between the absorptive power of the solutions and the dissociation could be established.

W. J. P.

Crystalline Liquids. By RUDOLF SCHENCK (*Zeit. physikal. Chem.*, 1898, 25, 337—352).—Certain para-azoxy-compounds, parazoxyanisole, for example, melt to a turbid liquid, which, at a higher temperature, becomes clear, and it was shown by Lehmann that, although this turbid liquid consists of liquid drops, yet it exhibits double refraction and behaves optically like a crystalline compound. When the temperature is raised, and the liquid becomes clear, these optical properties are lost; this temperature may hence be regarded as the transition temperature of the two liquids, and the author endeavoured to determine the molecular weight of the two liquids in the cases of parazoxy-

anisole, paraxylylene, and cholesteryl benzoate. By the dilatometric method, the transition temperatures for these compounds were found to be respectively 134° , 165.2° , and 178° , the last compound exhibiting but a very small density change. The molecular surface energy was determined by Ramsay and Shields' method, but only in the case of the cholesteryl benzoate was any indication obtained of a difference in the molecular weights of the two liquids. The molecular lowering of the transition temperature in the case of paraxylylene was 750.2 , from which, by the expression $0.02T^2/u$, the heat of transition is calculated as 4.42 cal. Mixtures of the compounds gave a transition temperature agreeing satisfactorily with that calculated by the mixture rule. The effect of pressure was calculated for paraxylylene by the expression $dt/dp = T(v^1 - v)/u$; to raise the transition point one degree requires about 13 atmospheres pressure.

L. M. J.

Action exerted by certain Metals and other Substances on a Photographic Plate. By WILLIAM J. RUSSELL (*Proc. Roy. Soc.*, 1897, 61, 424—433).—Becquerel (*Abstr.*, 1896, ii, 406) has shown that uranium and some of its salts act on a photographic plate, the action being rendered evident by the ordinary process of development. The author records some experiments which have been made to determine whether the uranium compounds lose their peculiar activity on being kept in the dark. No marked difference could be detected between samples kept in the light and those preserved in total darkness. In carrying out these experiments, and using a card painted with the yellow oxide of uranium, perforated zinc was used as a screen to show the activity of the uranium compound by the density of the picture of the pattern formed, but, in place of obtaining in all instances a negative of the perforated zinc, the reverse took place, and the greatest amount of action occurred underneath the zinc. From this it appeared that zinc itself must be able to effect a change of the same kind as the uranium, at all events, to act on a photographic plate, and further experiment with zinc alone proved this to be the case. Colson (*Abstr.*, 1896, ii, 601) has also described this action of zinc, and found that similar results can be obtained with cadmium and magnesium; he ascribes the action to vapour given off by these metals.

A large number of experiments were made with zinc under different conditions. The zinc must be clean and bright, as, in its ordinary condition, after exposure to the air, it ceases to be active. The salts also have no power of acting in this way. A polished piece of zinc laid on a highly sensitive photographic plate will, under certain conditions, even in 4 or 5 hours, so act on it that, on development, a complete picture of the zinc is produced, showing the scratches or any ruled lines or faint pattern drawn on it, or, if flaws in the metal exist, they are clearly seen.

Absolute contact of metal and plate is not necessary. If screens of different thicknesses of any inactive substance be interposed between plate and metal, thus preventing contact, the action still occurs; if the screen be very thin, a picture of the zinc surface is still obtained, but if thicker, only a dark, cloudy patch is formed. If a thick piece of

glass tubing an inch long be placed on a photographic plate, and the upper end covered with a piece of polished zinc, in a week to a fortnight distinct action will be found to have taken place below the zinc. The action is not transmitted through glass, even of the thinnest kind, but takes place readily through celluloid, sheet gelatin, gutta-percha tissue, collodion, vegetable and real parchment, goldbeater's skin, tracing paper, and, no doubt, many other substances. Certain writing papers are quite opaque to the action; with others, pictures of the structure and the watermark are easily obtained. A mere difference of colour does not appear to alter the absorptive power of a medium; at least, this is the case with gelatin.

In addition to cadmium and magnesium, many other metals and also certain alloys produce effects similar to that produced by zinc. The following is a rough list of active metallic substances approximately in the order of their activity:—mercury, magnesium, cadmium, zinc, nickel, aluminium, pewter, fusible metal, lead, bismuth, tin, cobalt, antimony. Mercury is at ordinary temperatures the most active metal, but the other metals do not follow in the order of their fusibility or exactly according to any obvious physical property, but most nearly according to their position in the electrical series. The action of mercury does not take place as readily through gelatin, but more readily through gutta-percha than is the case with zinc. Iron, gold, and platinum are not active, and copper only very slightly. These results are founded on experiments in which the exposure lasted one week; with longer exposure, other metals will probably produce some action.

Aqueous vapour is not apparently an active agent in producing these reactions. In an atmosphere of hydrogen, the action takes place as it does in air. Carbonic anhydride, under ordinary conditions, does produce an effect, but this probably arises from its action on the zinc plate. Alteration of temperature produces very marked effects, as in all cases increase of temperature causes increased action. Like glass, selenite, gum arabic and paraffin are impervious to the action. The behaviour of certain salts in the dry state was tried by soaking unglazed paper in different solutions, drying it, and then placing it, either with or without a screen, between the zinc and the photographic plate. Solutions of alum, potassium chromate, zinc sulphate, and quinine sulphate were found to render the paper quite opaque to the action of the zinc.

Some singular developments of this subject have arisen from experiments made while examining the metals. A piece of polished zinc was coated with copal varnish with the object of ascertaining whether the action would take place through this medium. The photographic plate, notwithstanding the varnish was strongly acted on, indeed the pictures were darker than those given by the zinc alone, and on trying the copal on plain glass instead of on zinc, it proved that effects apparently similar to those obtained with zinc were produced. Substances which are transparent or opaque to the action of the metals seem to act in the same way towards copal. Glass is perfectly impervious to its action, but celluloid, gutta-percha tissue, and gelatin it

permeates more readily than zinc does. It is rather more active than zinc. The activity of the copal varies considerably under different conditions. The fused gum is not so active as when picture varnish is used. Heating it in a water bath for a considerable length of time certainly deprives it of some of its activity; but this can be revived by wetting it with ether and allowing it to dry again at ordinary temperatures. As with zinc, increase of temperature increases its activity to a great extent.

Many other substances of the same nature as copal act in the same way. This has been proved to be the case with Damar and with Canada balsam, but copal seems to be the best representative of the class. Certain gums, such as gum arabic, gum senegal, have not the property of acting in this way. There are, however, a large number of substances which have the power of acting in a manner similar to the copal; one of these is wood, and it possesses a very considerable amount of activity. Any ordinary smooth piece of wood laid on a photographic plate will act like zinc in impressing its picture on the plate. Substances such as straw, hay, bamboo, oiled silk, and no doubt many others, act in the same way. If wood, however, is painted with melted paraffin it is no longer active. Ordinary charcoal also depicts itself on a photographic plate, but if it be heated for some hours in a covered crucible it loses this property. An ordinary piece of wood, if it be charred on one side by heating it with a Bunsen lamp, becomes remarkably active. The action passes readily through different media, such as gelatin, tracing paper and vegetable parchment, and the structure of the charcoal is shown, when the action has taken place, even through a sheet of vegetable parchment. Coal and coke, sulphur, sugar, on the other hand, exert no action of this kind. Printers' ink in most cases is not capable of acting, like copal, on a photographic plate, but there are many cases in which it is a remarkably active substance. Specially so is the ink used in printing many of the newspapers. Samples of strawboard from different sources have been tried, and all found to be active, and different substances of a like nature have been tried, such as brown papers, some of which are active, but none more so than common strawboard. Writing paper and white cardboard have not this power of acting on a photographic plate.

The action of the vapour from a few liquids on a sensitive plate has been tried. The plate was placed about half an inch above the liquid, and a screen, with holes cut in it, was fastened against the plate. Methylated spirit acted slightly on the plate; pure alcohol and ether had no action, but turpentine and oil of cloves produced a slight amount of action.

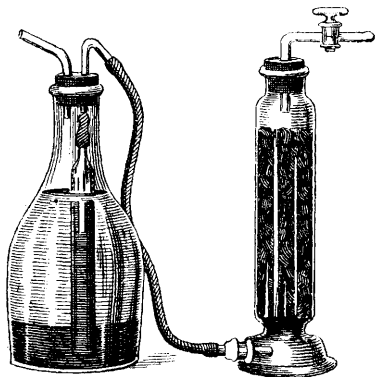
The supposition that all these active substances, the metals as well as organic compounds, give off a vapour capable of acting on a photographic plate, naturally suggests itself, and that copal does give off a vapour which directly or indirectly is active there can be no doubt. At the same time, it is difficult to suppose that this can be the case throughout, and further experiments, it is hoped, may lead to explanations not now evident.

It is only the most sensitive photographic plates which, without extremely long exposures, give the results described.

H. C.

Self-regulating Gas-generating Apparatus. By W. W. ANDREWS (*Chem. Zeit.*, 1897, 21, 666—667).—The apparatus consists of two parts, a reservoir filled, say, with acid, and a generator filled with the requisite material.

The former has the appearance of an ordinary wash-bottle, the longer tube of which penetrates but a short distance into the acid, and is sealed into a wider tube, open at the bottom and slightly perforated near the top; this reaches to the bottom of the acid.



The generator is merely an ordinary calcium chloride tower, connected by means of a long india-rubber tube with the reservoir. To set the apparatus going, the tap of the tower is opened, and a little acid is blown in from the reservoir; this starts the syphon, and more acid enters in consequence. When the tap is closed, the acid is forced back into the reservoir, and being now higher

in specific gravity, it sinks to the bottom. On reopening the tap, the syphon again acts, and fresh acid enters the tower. For acetylene, another kind of generating bottle, made of thin glass so as to withstand heat, is recommended.

L. DE K.

Inorganic Chemistry.

Preparation of Chemically Pure Hydrogen Sulphide for Laboratory Purposes. By JOSEF R. MICHLER (*Chem. Zeit.*, 1897, 21, 659).—The author recommends using a solution of calcium sulphide to obtain a hydrogen sulphide absolutely free from arsenic. A solution of sp. gr. = 1.16 is capable of yielding 110 times its volume of the gas when treated with hydrochloric acid. L. DE K.

[**Chemical and Physical Properties of very Concentrated Nitric Acid.**] By VICTOR H. VELEY and J. J. MANLEY (*Proc. Roy. Soc.*, 1897, 62, 224—225).—See this vol., ii, 277.

Densities of Carbonic Oxide, Carbonic Anhydride, and Nitrous Oxide. By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1897, 62, 204—209).—The observations were carried out by the method and with the apparatus described in a former paper (*Abstr.*, 1893, ii, 514). Carbonic oxide was prepared from potassium ferrocyanide, from oxalic acid, and from sodium formate. The density found was 27.9989 ($O=32$), and if equal volumes may be taken as accurately representative of CO and of O_2 , the atomic weight of carbon will be 11.9989

(O = 16). Carbonic anhydride from marble and hydrochloric acid gave the weight 3·6349, and nitrous oxide prepared from ammonium nitrate, or obtained from the commercial liquefied gas, gave 3·6359, corresponding with 2·6276 for oxygen.

The following summary gives the densities of the various gases relatively to air, all obtained by the same apparatus. The last figure is of little significance.

Air, free from H ₂ O and CO ₂	1·00000	Argon	1·37752
Oxygen	1·10535	Carbonic oxide	0·96716
Nitrogen and argon (atmospheric)	0·97209	Carbonic anhydride	1·52909
Nitrogen	0·96737	Nitrous oxide	1·52951

The value obtained for hydrogen on the same scale was 0·06960; but the researches of Leduc and Morley appear to show that this number is a little too high.

H. C.

Formation of Metallic Sodium from Sodium Peroxide. By HEINRICH BAMBERGER (*Ber.*, 1898, 31, 451).—Metallic sodium is readily formed when a mixture of sodium peroxide with charcoal, coke, or graphite is heated at 300—400° in a covered crucible. The reaction, which is a very violent one, must only be carried out with small quantities, and can be used as a lecture experiment, the sodium being found after the experiment on the cover and the cool upper portion of the sides of the crucible. The reduction can also be effected by means of calcium carbide, the reaction then being even more violent than when carbon is used.

A. H.

Coloured Haloid Salts of the Alkali Metals. By EILHARD WIEDEMANN and GERHARD C. SCHMIDT (*Ann. Phys. Chem.*, 1898, [ii], 64, 78—91).—The authors have investigated the colour changes taking place in the haloid salts of the alkali metals under the influence of the cathode discharge, already noticed by Goldstein (*Abstr.*, 1895, ii, 150) and others. They find that the coloured product always has an alkaline reaction, and that in physical and chemical properties it is identical with the substance obtained by treatment of the haloid salt with the alkali metal. The colour change must, therefore, be regarded as due to the formation of a subchloride, or solution of the free metal in the haloid salt.

H. C.

Baker's Research on the Non-combination of Dry Hydrogen Chloride and Ammonia; Vapour Density of Dry Ammonium Chloride. By S. GUTMANN (*Annalen*, 1898, 299, 267—286).—The author has repeated Baker's experiments (*Trans.*, 1894, 65, 611) relative to the effect exerted by water on the combination of hydrogen chloride with ammonia, but the results of his investigation do not confirm those of Baker.

In the first place, he shows that dry hydrogen chloride is absorbed by phosphoric anhydride; the drier the gas, the more slowly does absorption proceed, advancing more rapidly with time, then finally becoming retarded. It is also found that dry ammonia is absorbed by phosphoric anhydride.

The author's experiments indicate that complete desiccation of

hydrogen chloride and ammonia is powerless to prevent combination, although the action is much retarded, and is rendered less energetic.

Determination of the vapour density of carefully dried ammonium chloride gave results concordant with complete dissociation (compare, however, Baker, *Trans.*, 1898, 422). M. O. F.

Ammonium Peroxide. By PETR. G. MELIKOFF and L. PISSARJEVSKY (*Ber.*, 1898, 31, 446—449. Compare this vol., ii, 161, 219).—When an ethereal solution of ammonia and hydrogen peroxide is cooled to -40° , a granular, crystalline mass is deposited which has the composition $(\text{NH}_4)_2\text{O}_2 + \text{H}_2\text{O}_2$, and readily decomposes at -40° into ammonia and hydrogen peroxide; the crystals are isotropic and appear to be cubes. At the ordinary temperature, the compound decomposes into ammonia and oxygen according to the equation $(\text{NH}_4)_2\text{O}_2 + \text{H}_2\text{O}_2 = 2\text{NH}_4 \cdot \text{OH} + \text{O}_2$, a trace of ammonium nitrite being simultaneously formed; in an aqueous solution, a similar decomposition occurs, the amount of nitrite formed increasing with the degree of dilution and with the temperature.

The evolution of oxygen which takes place when ammonia and hydrogen peroxide are brought together in solution, is therefore due to a reaction between ammonium peroxide and hydrogen peroxide, precisely similar to that which occurs when sodium peroxide and hydrogen peroxide are mixed. A. H.

Duration of the Phosphorescence of Strontium Sulphide. By JOSÉ R. MOURELO (*Compt. rend.*, 1897, 125, 1098—1100).—When the different modifications of strontium sulphide (*Abstr.*, 1897, ii, 450 and 469) are exposed to light under similar conditions, the intensity of the phosphorescence increases in the following order. (A) Prepared by the reduction of the sulphate by charcoal; (B) by the action of sulphur on the carbonate; (C) by the action of hydrogen sulphide on the oxide; (D) by Verneuil's method for preparing calcium sulphide, and (E) the author's modification of Verneuil's method. The length of time during which the sulphides retain their phosphorescence increases in the same order; A and B ceased to phosphoresce after 3 hours, whilst E was still phosphorescent, although feebly, after 12 hours. When the time of exposure of the sulphide to light is increased, the colour and intensity of the phosphorescence is not affected, but its duration is materially prolonged.

The minimum time required to excite phosphorescence is least in the case of E and greatest in the case of A; it follows the inverse order of the intensity and duration. With E, a second's exposure to diffused light is sufficient to set up distinct phosphorescence.

Temperature, up to 50° , has no appreciable influence on the intensity of the phosphorescence, but prolonged exposure to direct sunlight slightly reduces the intensity. On the other hand, insolation markedly reduces the minimum exposure required to excite phosphorescence, but this effect gradually disappears and the sulphide returns to its original condition as regards sensitiveness. C. H. B.

Alloys of Beryllium and Copper. By PAUL LEBEAU (*Compt. rend.*, 1897, 125, 1172—1174).—Metallic beryllium cannot be obtained by

the action of the electric arc on a mixture of the oxide and carbon or of the oxide and the carbide, most probably owing to the great readiness with which beryllium and carbon combine at high temperatures. Alloys of beryllium with other metals can, however, readily be prepared by reducing beryllium oxide in presence of a metal or a metallic oxide. When a very intimate mixture of copper and beryllium oxides (such as is obtained by the action of heat on the mixture of nitrates obtained by dissolving the two oxides, in any desired proportions, in nitric acid) is heated with carbon for five minutes with an arc from a current of 900 ampères and 45 volts, the product is red, brittle, and non-homogeneous; when liquated, it yields the pure beryllium-copper alloy, and leaves a crystalline mass of a double beryllium copper oxide.

The alloys that contain 10 per cent. of beryllium are pale yellow, almost white; those with 5 per cent. are yellower, can be filed and polished readily, and are malleable when hot or cold. They do not alter in the air, but tarnish slightly in presence of hydrogen sulphide, and are readily dissolved by nitric acid. From these alloys, others containing a definite, but lower, proportion of beryllium can readily be prepared by melting them with the necessary proportion of copper. Even so low a proportion of beryllium as 0.5 per cent. distinctly alters the appearance of the copper, and makes it very sonorous. An alloy containing 1.32 per cent. of beryllium is golden yellow, highly sonorous, and can readily be filed and forged.

Alloys of beryllium with the common metals and with chromium, molybdenum, tungsten, and some other refractory metals have been prepared and will be described later.

C. H. B.

Cadmium Compounds. By FRANCESCO CANZONERI. (*Gazzetta*, 1897, 27, ii, 486—492).—On heating cadmium with cadmium chloride, in the hope of obtaining a cadmium subchloride, the author obtained a small proportion of a grey powder the composition of which depends on the composition of the mixture of cadmium and cadmium chloride used. If cadmium chloride is in excess, the grey powder has practically the composition $2\text{CdO}, \text{CdCl}_2$; a similar product is formed, with development of heat, as a heavy, white powder on fusing a mixture of cadmium oxide and chloride in the requisite proportion. If cadmium is in excess, the product contains more cadmium than is required for the composition $2\text{CdO}, \text{CdCl}_2$.

W. J. P.

Microchemical Examination of Alloys. By JOHN E. STEAD (*J. Soc. Chem. Ind.*, 1897, 16, 200—208; 506—509).—Lead-antimony alloys containing less than 12.5 per cent. of antimony appear to be perfectly homogeneous after solidification, but with a higher percentage of antimony, crystals of that metal separate throughout the mass, and rise to the surface, leaving the eutectic alloy of the composition Pb_4Sb , which has a solidifying point of 247° , and sp. gr. = 10.48. This solidifies in spherulites, radiating from nuclei, and during solidification splits up into laminae of its constituent metals. The solidified eutectic alloy of lead and tin consists of similar masses of spherulites. From alloys of tin and antimony, cubical crystals of the

composition SnSb separate, but the compound seems only to form in presence of a considerable excess of tin.

The papers contain much valuable information respecting other alloys, and are illustrated with microphotographs of the appearance of polished and etched surfaces.

M. J. S.

Cerium. By O. BOUDOUARD. *Compt. rend.*, 1897, 125, 1096—1097.—A reply to Wyruboff and Verneuil. (This vol., ii, 222).

Atomic Weight of Cerium. By GRÉGOIRE N. WYRUBOFF and AUGUSTE V.-L. VERNEUIL. (*Compt. rend.*, 1897, 125, 1180—1181).—A continuation of the discussion with Boudouard (preceding abstract). In the authors' experiments, the maximum atomic weight obtained was 92.85 and the minimum 92.49. They point out that, although pure cerium oxide is white, the mere absence of colour is not of itself any guarantee of complete purity.

C. H. B.

Impurities of Aluminium and its Alloys. By ED. DEFACQZ (*Compt. rend.*, 1897, 125, 1174—1177).—When aluminium is dissolved in dilute hydrochloric acid (1:5) the residue is impure silicon, containing silica and aluminium, and ferric oxides, with traces of copper. An alloy of aluminium with 3 per cent. of copper, when dissolved in dilute aqua regia, also yields impure silicon containing 5 per cent. or more of copper oxide. The same alloy when dissolved in hydrochloric acid (1:10), yields a non-homogeneous residue of copper mixed with silicon, iron, and aluminium. All these residues oxidise very readily, even on the filter. It is noteworthy that, when the aluminium and its alloys are dissolved in dilute acids, the impurities divide themselves unequally between the solution and the residue.

C. H. B.

Chromous Sodium Carbonate. By GEORGES BAUGÉ. (*Compt. rend.*, 1897, 125, 1177—1180).—When well washed and moist chromous acetate is mixed with a solution of sodium carbonate, it first dissolves and after a time a reddish-brown compound separates; this is washed with water, and afterwards with alcohol of 98°, all the operations being conducted in an atmosphere of carbonic anhydride. After drying in a current of carbonic anhydride, it has the composition $\text{CrNa}_2(\text{CO}_3)_2 + 10\text{H}_2\text{O}$, and forms microscopic, tabular lozenge-shaped crystals which lose water in a vacuum at the ordinary temperature or at 100°. It is very soluble in cold water, but the solubility gradually diminishes, probably in consequence of polymerisation. It is a powerful reducing agent, and decomposes water at a little below 100° with liberation of hydrogen and formation of a compound that will be described later. When exposed to dry air, it effloresces, and is afterwards converted into a mixture of sodium carbonate and chromic hydroxide; in moist air, it oxidises rapidly with development of heat. Chlorine converts it into chromic oxide with liberation of carbonic anhydride; hydrogen and hydrogen sulphide have no action on it in the cold, and when heated at 100° in a current of these gases, it yields the monhydrate. Dilute hydrochloric and sulphuric acids dissolve the salt, forming blue solutions.

The monhydrate, $\text{CrNa}_2(\text{CO}_3)_2 + \text{H}_2\text{O}$, is prepared from the decahydrate by the action of a current of a dry inert gas at 100°. It

is a yellow powder which becomes brown when heated in a vacuum or a current of hydrogen, but regains its yellow colour on cooling. At 300° , it decomposes into sodium carbonate and chromic oxide. When heated in air, it is converted into sodium chromate; when heated in chlorine, it yields chromyl dichloride and chromic oxide; in hydrogen sulphide at about 240° , it yields the red, crystalline sulphide described by Moissan. Its other properties are practically identical with those of the decahydrate.

C. H. B.

Alkali Salts of Perchromic Acid. By O. FRITZ WIEDE (*Ber.*, 1898, 31, 516—524. Compare this vol., ii, 28).—By the action of ammonia under certain conditions on an ethereal solution of perchromic acid, there is formed a substance of the formula $\text{NH}_4\text{CrO}_5 + \text{H}_2\text{O}_2$; this is a violet-black, crystalline powder, and may be preserved for several days in a cold situation if protected from moisture. When kept for some time, it becomes superficially yellow, and when exposed to air passes completely into ammonium dichromate within 24 hours. The solution in ice-cold water is violet-brown, and neutral to test paper; the concentrated solution rapidly decomposes, yielding oxygen and ammonium dichromate. Ammonia converts the substance into the compound of chromium tetroxide and ammonia (*loc. cit.*); dilute sulphuric acid gives rise to an indigo-blue solution. Barium chloride and lead acetate give violet-brown precipitates, which, after liberating gas, pass into the yellow chromate; silver nitrate yields a brownish-violet turbidity, which immediately changes into the reddish-brown silver chromate. Ferric chloride develops a grass-green coloration, whilst ferrous sulphate liberates gas and forms a yellow solution; potassium permanganate forms a blood-red solution, which yields oxygen and manganese dioxide when acidified.

By means of alcoholic potash at -5° , the corresponding potassium compound, having the formula $\text{KCrO}_5 + \text{H}_2\text{O}_2$, has been obtained as a violet, indefinitely crystalline powder; it is highly explosive, and begins to decompose in the process of desiccation. In aqueous solution, it behaves like the ammonium compound.

The author regards the hydrogen peroxide in the foregoing compounds as hydrogen peroxide of crystallisation. In an ethereal solution of perchromic acid, the latter is not in combination with hydrogen peroxide.

M. O. F.

Rare Earths. By LUDWIG HABER (*Monatsh.*, 1897, 18, 687—699).—*Thorium chromate*, $\text{Th}(\text{CrO}_4)_2 + 3\text{H}_2\text{O}$, is precipitated as an orange-yellow, crystalline powder when a solution of thorium nitrate is boiled for some time with chromic acid, or, better, with potassium or sodium dichromate; under similar conditions, cerium, lanthanum and didymium salts, however, give no precipitate, whilst zirconium forms a *basic chromate*, the composition of which varies with the mode of preparation.

When a solution of a thorium salt to which sodium acetate has been added is well boiled, a brilliantly white, crystalline precipitate of *basic thorium acetate*, $\text{Th}(\text{OAc})_2(\text{OH})_2 + \text{H}_2\text{O}$, is formed. Since cerium, lanthanum and didymium are not precipitated at all under the same conditions, this reaction affords an easy method of preparing thoria

free from these metals; zirconium is, however, precipitated as a *basic acetate* of indefinite composition.

Whilst cerium, lanthanum, and didymium salts are precipitated by sodium formate as normal formates, the salts of thorium and zirconium give rise to crystalline, *basic formates* of varying composition.

The precipitate formed on adding tartaric acid to a solution of thorium chloride appears to have the composition, $C_4H_4O_7Th(OH)_2$, not $(C_4H_4O_6)_4Th_3(OH)_4 + 5H_2O$, as stated by Cleve (this Journal, 1875, 236). Cerium, lanthanum and didymium are not precipitated by tartaric acid, whilst zirconium gives rise to a salt of varying composition.

A *basic thorium citrate*, $C_6H_5O_7Th \cdot OH$, is formed as a white, flocculent precipitate on heating a solution of thorium chloride with citric acid.

Thorium malate, $(C_4H_4O_5)_3Th_2(OH)_2$, is a white, crystalline powder which is almost insoluble in water.

W. A. D.

Mineralogical Chemistry.

Steenstrupine. By JOH. CHR. MOBERG (*Zeit. Kryst. Min.*, 1898, 29, 386—398).—Steenstrupine, first described by Lorenzen (Abstr. 1883, 960), has only been found in the nephelite-syenite at Kangerdluarsuk in West Greenland; it has been placed by Brögger in the melanocerite group. The following new analyses have been made by Blomstrand: I, on crystalline material of sp. gr. = 3·4009, carefully separated from enclosed ægirite; II and III, on massive, and more altered material. None of these lead to simple formulæ; with the exception of the presence of beryllium and phosphoric acid, analysis I agrees with that made by Lorenzen. The black, rhombohedral crystals are tabular in habit, and the faces are somewhat rough and rounded; the axial ratio, $a:c = 1:1\cdot0842$, is near to that of eudialyte, but quite different from that of melanocerite. The mineral is optically negative; thin sections show variations in the strength of the double refraction, and other signs of alteration.

	SiO ₂ .	Ta ₂ O ₅ , Nb ₂ O ₅ ,	P ₂ O ₅ .	ThO ₂ .	Ce ₂ O ₃ .	La ₂ O ₃ , Di ₂ O ₃ .	Y ₂ O ₃ .	Fe ₂ O ₃ .
I.	26·57	1·21	5·81	3·03	14·40	15·90		4·55
II.	20·61	1·58	4·53	3·84	17·03	15·52	2·19	5·18
III.	21·30	1·02	4·39	4·13	18·50	16·68	1·68	4·91

	Mn ₂ O ₃ .	Al ₂ O ₃ .	BeO.	CaO.	PbO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	4·40	2·55		4·03	0·46	8·34	0·50	7·58	99·33
II.	5·79	0·40	1·22	4·22	1·02	2·53	—	12·73	98·39
III.	6·80	0·60	1·93	4·55	0·78	2·54	—	10·30	100·11

The mineral is decomposed by hydrochloric acid, giving a dark brown solution which evolves chlorine. Crystalline material with a

pale yellow streak and sp. gr. = 3·4733, gave off chlorine corresponding with 0·184 per cent. of active oxygen; in anal. I, this gives Mn_2O_3 , 1·82, and MnO , 2·32 per cent. The more altered massive material with a dark brown streak, sp. gr. = 3·1901, and SiO_2 , 21·59; H_2O , 13·39 (of this 4·64 was lost at 100—110°), contained 1·48 per cent. of active oxygen, which is enough to convert all the manganese and cerium in II and III into Mn_2O_3 and CeO_2 respectively. L. J. S.

[Microcline from Bohemia]. By FRIEDRICH KATZER (*Jahrb. f. Min.*, 1898, i. Ref. 72; from *Oesterr. Zeit. Berg- u. Hüttenwesen*, 1896, 44).—In a description of the felspar industry in Bohemia, the following analysis is given of greyish-green to green microcline, from Kloub near Protivin.

SiO_2 .	Al_2O_3 .	CaO .	K_2O .	Na_2O .	MgO .	Loss on ignition.	Total.
63·22	18·96	—	16·02	1·94	0·12	0·33	100·59.

L. J. S.

Alpine Cordierite-pinite. By HERMANN GEMBÖCK (*Zeit. Kryst. Min.*, 1898, 29, 305—332).—The general term pinite includes a large number of alteration products of cordierite, felspar, nephelite, and other minerals; under the name cordierite-pinite, the author considers only those which have been derived from cordierite. Under the microscope, these are seen to consist mainly of muscovite and chlorite, with a little quartz, biotite, limonite, kyanite, epidote, and garnet. Only a portion is soluble in hydrochloric acid, the soluble portion containing aluminium and iron with a little calcium and magnesium. Material from the Alps is described; lists of crystal forms, &c., and a review of the literature are given. L. J. S.

Mineral Water from S. Omobono in the Imagna Valley. By GIACOMO CARRARA (*Gazzetta*, 1897, 27, ii, 559—571).—The old spring of S. Omobono issues from a black, schistose rock, containing pyrites, in the Imagna valley, about 23 kilometres from Bergamo; the water, which has been considered efficacious in cases of skin diseases, issues at a temperature never exceeding 13°, and has an odour of hydrogen sulphide. It has the sp. gr. = 1·00026 at 9·5°, and contains traces of copper, arsenic, aluminium, and phosphoric acid. The analytical results show that the water contains the constituents stated in grams per litre in the accompanying table.

Substance.	Percentage.	Substance.	Percentage.
LiCl	0·00003	$\text{Ca}(\text{HCO}_3)_2$	0·28000
NH_4Cl	0·00004	$\text{Mg}(\text{HCO}_3)_2$	0·19237
NaCl	0·00216	$\text{Fe}(\text{HCO}_3)_2$	0·00033
NaI	0·00005	SiO_2	0·01144
BaSO_4	0·00035	TiO_2	0·00001
SrSO_4	0·00707	CO_2 (free)	0·07468
K_2SO_4	0·01153	H_2S	0·00601
Na_2SO_4	0·07031	N_2 (free)	0·01488
NaHCO_3	0·03864	Organic matter ...	0·03117

The bacteriological examination shows the water to be of a high degree of purity; plate cultivations gave colonies of *Bacillus fluorescens liquefacens*, *Tamnidium elegans*, *Mucor mucedo*, and white water bacilli.

W. J. P.

Physiological Chemistry.

Evolution of Gases During Pancreatic Digestion. By FERDINAND KLUG (*Pflüger's Archiv.*, 1898, 70, 329—345).—In 1874—1875 Hüfner (*J. prakt. Chem.*, 10, 1; 11, 43), and in 1881 Wassilieff (*Zeit. physiol. Chem.*, 6, 112) stated that various gases, especially carbonic anhydride, were evolved during pancreatic digestion when the activity of bacteria are excluded. Since then the opinion has, however, been generally held that the formation of such gases is due to micro-organisms. In the present research, the old statement of Hüfner is confirmed; small quantities of carbonic anhydride, and in some cases of hydrogen also, are formed when bacterial action is excluded by disinfectants like thymol. It, however, only takes place when fat is the substance acted on; it does not occur with glycerol, so the gases are considered to originate from the decomposition of the fatty acid radicles. W. D. H.

Absorption in the Small Intestine. By RUDOLF HÖBER (*Pflüger's Archiv.*, 1898, 70, 624—642).—Hypertonic, isotonic, and hypotonic solutions of salt in blood-serum are absorbed in the small intestine. The hyper- and hypo-tonic solutions become, in the course of absorption, isotonic. Isotonic solutions of different salts are absorbed at different rates; dealing with solutions so dilute that the salts are almost completely dissociated electrolytically, the difference in their behaviour depends on the properties of their ions. Of the kation ions, K, Na, and Li are almost equally quickly absorbed, NH_4 and urea more quickly, Ca more slowly, and Mg slowest of all. Ba, on account of its injurious action on the intestine, could not be observed. Of the anion ions, Cl is the most rapidly absorbed, then follow, in the order named, Br, I, NO_3 , SO_4 . From the behaviour of the NH_4 and urea, the conclusion is drawn that the cells of the intestine in their permeability resemble blood-corpuscles and plant cells. From the behaviour of Mg and SO_4 , the use of sulphates, and especially of magnesium sulphate, as purgatives becomes intelligible. W. D. H.

Action of Salts on Blood Corpuscles. By SVEN G. HEDIN (*Pflüger's Archiv.*, 1898, 70, 525—543).—Ammonium sulphate, phosphate, tartrate, and succinate, when added to blood in small quantities (0.05 gram-molecule per litre), divide themselves equally between corpuscles and plasma, whilst larger quantities (0.1) enter partly into the corpuscles, but remain principally in the plasma. The fraction which remains in the plasma increases with the amount of salt added

up to 0.3 gram, and in those concentrations, where there is excess of salt in the plasma, the volume of the corpuscles diminishes.

Ammonium chloride, bromide, nitrate, thiocyanate, oxalate, ferrocyanide, ferricyanide, lactate, and ethylsulphonate distribute themselves equally in plasma and corpuscles at all concentrations.

The corresponding salts of trimethylamine, ethylamine, and, probably, of other nitrogenous bases, may be divided into the same two groups, corresponding with those of ammonium just described.

W. D. H.

Acids obtained by the Hydrolysis of the Fat of the Dog-fish. By EUGEN LJUBARSKY (*J. pr. Chem.*, 1898, [ii], 57, 19—27).—On hydrolysing the fat of the Caspian dog-fish, no volatile acids were obtained, but a mixture of 17 per cent. of palmitic acid with 83 per cent. of liquid unsaturated acids. The latter portion, on oxidation with alkaline potassium permanganate, gave rise to a mixture of dihydroxystearic and dihydroxypalmitic acids, and thus consisted of a mixture of oleic acid and physetoleic acid, the latter being present in the greater proportion.

W. A. D.

Effect of Feeding with Beet and Dried and Sour Diffusion-chips on Milk Production. By OSCAR KELLNER and G. ANDRÁ (*Landw. Versuchs.-Stat.*, 1898, 49, 401—418).—Twenty-four cows were fed during four periods of 20 days on a ration of grass, oat-straw, bran, cotton meal, and earth-nut meal, with the addition of (1 and 4) roots, 50 kilos.; (2) dry diffusion-chips, 8 kilos.; (3) sour chips, 78 kilos. per 1000 lbs. live weight. The results of the experiments show that the replacement of 27.5 kilos. of roots by 4.4 kilos. of dried chips increased the yield of milk by 0.953 kilo., whilst the replacement by 41.8 kilos. of sour chips increased the yield by 1.721 kilos. per cow of 550 kilos. live weight. The weight of the cows was, on the whole, greatest during the feeding with diffusion-chips. The composition of the milk was not essentially altered.

N. H. J. M.

Yield and Composition of Sow's Milk. By WILLIAM A. HENRY and FRITZ W. A. WOLL (*Ann. Rep. Agr. Exper. Stat. Univ., Wisconsin*, 1897, 14, 10—19).—The amount of milk yielded by several sows was ascertained by keeping the pigs by themselves and placing them with the sows at suitable intervals, weighing them before and after feeding. The weighing was continued for 3 days in each case, and the experiment was repeated at intervals of two weeks. During the period between farrowing and weaning, the average daily yields of the four sows were 5.8, 4.1, 5.4, and 5.5 lbs.

Analyses of seven samples of sow's milk gave the following percentage results.

	Water.	Fat.	Cascin and albumin.	Milk-sugar.	Solids not fat.	Ash.
Average.....	80.96	7.06	6.20	4.75	11.99	1.07
Lowest	79.5	3.9	5.3	3.1	10.8	0.8
Highest	82.9	9.5	7.3	6.0	13.2	1.3

Sp. gr. (average of 5 samples) = 1.0389.

When compared with the results given by König, the greatest

difference is seen to be in the amount of fat and sugar (compare also Rohde, Schweinezucht, 1892, 256), but the results (for fat) correspond with those obtained by Petersen and Oetken, and König's and Rohde's figures are certainly too low, and the conclusions based on them entirely wrong. The average amount of fat (including all the available results mentioned, 64 samples) is 6.74 per cent.; a sow giving 5 lbs. of milk would therefore yield about 0.34 lb. of fat a day, a considerable amount for an animal only about one-third the weight of an average cow.

N. H. J. M.

Iodothyryn and Atropine: Sodium Iodide and Muscarine. By E. VON CYON (*Pflüger's Archiv*, 1898, '70, 511—512; 634—644).—If a rabbit is atropinised so that stimulation of its vagus produces no inhibition of the heart, the administration of iodothyryn neutralises momentarily this effect. This action of iodothyryn on the heart nerves confirms the previous opinion expressed by the author on the importance of the thyroid in relation to the heart.

Sodium iodide is antagonistic to iodothyryn; the question arises, is it also antagonistic to muscarine which has a stimulating action on the vagus endings? The answer is, yes. The experiments were made on rabbits. If sodium iodide is injected intravenously, it prevents the subsequent action of muscarine, and muscarine prevents the paralysing action of sodium iodide on these nerve-endings from taking place.

W. D. H.

Formation of Fat during Phosphorus Poisoning.—By OSVALDO POLIMANTI (*Pflüger's Archiv*, 1898, '70, 349—365).—This investigation was undertaken with a view to the elucidation of the much debated question whether fat may originate in the organism from proteid; the result gives an answer to this question in the affirmative. The central nervous system has no part in the changes produced by poisoning with phosphorus. The frogs used were free from glycogen. Not only fat, but also water, increases in the organs under these circumstances.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation without Yeast Cells. By EDUARD SCHUNCK (*Ber.*, 1898, 31, 309. Compare this vol., ii, 127).—In 1854, the author showed that erythrozyme, the madder ferment, is capable of producing alcoholic fermentation of a sugar solution; a mixture of hydrogen and carbonic anhydride is set free, and a small quantity of succinic acid produced. M. O. F.

Formation of Nitrates. By ALBERT STUTZER and R. HARTLEB (*Chem. Centr.*, 1897, i, 330; from *Centr. Bakt. Par.*, 1896, 2, ii, 701).—A mould fungus which forms a branched mycelium and macro- and micro-spores was found to take part in nitrification. Its action varies with the degree of development, and the nature of the nutritive

solution and the presence or absence of air are of importance. Under certain conditions, the fungus lives on organic nitrogen and induces nitrification; under other conditions, nitrites and nitrates respectively are produced.

N. H. J. M.

The Nitric Organism. By ALBERT STUTZER and R. HARTLEB (*Chem. Centr.*, 1897, i, 554—555, and 1243—1244; from *Centr. Bakt. Par.*, 1897, 3, i, 6—9, 54—57, and ii, 161—177).—When the nitric organism has been growing in a liquid culture-medium for some time, and a considerable proportion of nitrite has been converted into nitrate, as Winogradsky has pointed out, the mycelium of a mould-fungus appears on the surface of the liquid. This fungus appears to be a modification of the original nitric organism, and is formed when air, free from carbonic anhydride, is passed through a test-tube containing a pure culture of the organism in a solution of sodium nitrite containing glycerol. The morphological properties of the nitric organism are, on the other hand, not changed when it is cultivated in a solution of nitrite through which atmospheric carbonic anhydride is passed; in the latter case, therefore, no mould-fungus is formed.

The authors describe the morphology of the fungus. It is best cultivated at 20—30° on agar-agar plates, with a substratum containing asparagine, peptone, sodium nitrite, sodium nitrate, urea, and ammonium sulphate. Special attention is directed to the white incrustation (*Kreideweisse Auflagerung*) that is formed by the development into hyphæ of the gonidia after they become detached from the sterigma. The hyphæ produced are not fertile, but break up into short rods, which produce spores. Under very favourable conditions, the "incrustation hyphæ" can be converted into the fungus from which they originated; under unfavourable circumstances, they give rise to a modification which cannot be distinguished from *Cladothrix*.

W. A. D.

Reduction of Nitrates by Bacteria, and consequent Loss of Nitrogen. By ELLEN H. RICHARDS and G. W. ROLFS (*Chem. Centr.*, 1897, i, 424—425; from *Tech. quart.*, 9, 40—59, and *Centr. Bakt. Par.*, 2, ii, 709—710).—In presence of decomposable, non-sterilised organic matter, and in absence of sufficient dissolved oxygen for the growth of the bacteria, the oxygen of nitrates is utilised by the bacteria, and the nitrates reduced to nitrites or to nitrogen. The reduction of nitrates in irrigated soil may be considerable, and to avoid it, water should only be allowed to flow over the land in thin layers, so as not to prevent aëration.

Some ferments seem, in spite of aëration, to assimilate most readily the oxygen of nitrogenous compounds, and loss of nitrogen cannot be avoided when solutions containing certain organic compounds are applied to land containing nitrates.

N. H. J. M.

Euglena Sanguinea. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1898, 24, 360—363).—The deep brown-red pigment of this flagellate can be dissolved out with alcohol, and on evaporating the alcohol, octahedral crystals are obtained; they sinter at 103° and melt at 105°, are coloured blue by 50 per cent. sulphuric acid, and green by 50 per cent. nitric acid. An ethereal solution gives one absorption band in

the green. The pigment is not the same as bacterio-purpurin, which gives three absorption bands. The organism also contains paramylum granules.

W. D. H.

Effect of Chemical Agents and of Light on Germination. By A. J. J. VANDEVELDE (*Chem. Centr.*, 1897, i, 822—823; from *Bot. Centr.*, 69, 237—342).—In order to ascertain the effect of chemical agents on germination, seeds of *Pisum sativum* were kept for 24 hours in different solutions. Pure water did not alter the power of germinating, but the energy of germination was not inconsiderably accelerated. In presence of dissolved substances, the power and the energy of germination decreased as the strength of the solutions increased, up to a certain point of concentration; beyond this point, the effect of the solution diminished the nearer its strength approached saturation. In saturated solutions, the seeds did not swell. This diminished effect in strong solutions is attributed to the lessened power of diffusion.

The nitrates of potassium, sodium, ammonium, calcium, barium, and strontium are more injurious than the corresponding chlorides, and the sulphates of potassium, sodium, and ammonium less injurious than the chlorides and nitrates.

With potassium and sodium salts, the power and the energy of germination are similarly affected when the metal is the same.

Contrary to what would be expected, judging by their effect on the animal organism, barium and strontium salts are less injurious to germination than calcium salts. Potassium chlorate is only slightly injurious during the first stages, and the perchlorate is still less so; but potassium chromate and dichromate, and copper and iron sulphates are extremely injurious.

With regard to the effect of light, experiments made with a variety of seeds showed that germination was not affected by the presence or absence of light.

N. H. J. M.

Effect of Formaldehyde on Germination. By WILHELM KINZEL (*Landw. Versuchs.-Stat.*, 1898, 49, 461—466).—The object of the investigation was to ascertain whether formaldehyde is suitable for destroying the smut of grain crops, or whether it would prove injurious to the germinating power of the grain. Rye, wheat, oats, barley, clover, and lupins were treated with 0·1, 0·2 and 0·5 per cent. formaldehyde solutions for $\frac{1}{2}$, 1 and 2 hours. It was found that 0·1 per cent. formaldehyde (for 1 hour) was without injury to the seeds, whilst it almost entirely destroyed spores obtained from oats.

Dilute solutions of formaldehyde undergo less change than was supposed; 0·1 per cent. solutions, kept for 10 days, showed their full effect on spores, whilst a 40·8 per cent. solution still contained 38·4 per cent. of formaldehyde when kept for 14 months.

N. H. J. M.

Dependence of the Functions of Chlorophyll on the Chromatophores and on the Cytoplasm. By LEOPOLD KNY (*Ber. deut. bot. Ges.*, 1897, 15, 388—403).—Whilst Boussingault (*Agronomie*, 4, 317) and Jodin (*Abstr.*, 1886, 476) found that chlorophyll

can no longer assimilate the carbon of carbonic anhydride in absence of the chromatophores, Regnard (Abstr., 1886, 254) obtained results indicating that this property of chlorophyll is independent of the vegetable cell. In Regnard's experiments, however, the blue coloration did not appear for two or three hours; and Jodin (*loc. cit.*, p. 648) and Pringsheim (*Ber. deut. bot. Ges.*, 1886, 4) have thrown doubt on the suitability of the reagent he employed. In the experiments now described, a suitable solution for qualitative purposes was prepared as follows. Hydrogen sodium sulphite (about 30 grams) was dissolved in tap water (100 c.c.), zinc dust added, the whole shaken for 5 minutes, and diluted with 5 to 10 parts of water. After being filtered, the solution is treated with rather thick milk of lime until slightly alkaline, and allowed to settle. When indigo-carmin is added to the solution until it is still just decolorised, the mixture has a yellowish tint. Jodin's statement (*loc. cit.*) that the Coupier blue preparation acquires a blue colour when exposed to sunlight, also holds good for the indigo-carmin solution, but this is overcome by heating the preparation to boiling, before exposure to sunlight, quickly closing the vessel. The solution may then be exposed to sunlight for several days without change. Experiments made with the above solution showed clearly that chlorophyll cannot decompose carbonic anhydride when the enclosing cells are killed, or when extracted from a living plant and deposited on filter paper; similar results were obtained with Engelmann's bacteria-method.

According to Engelmann (*Ber. deut. bot. Ges.*, 1881, 446), isolated chlorophyll grains less than 0.005 mm. in diameter continue for a long time, in presence of light, to give off oxygen. The same result was obtained by Haberlandt (comp. Pfeffer, *Ber. Math.-Phys. Classe k. Sächs. Ges. Wiss. Leipzig*, 1896, 314). The author's experiments made with chlorophyll grains from many different sources give a decided negative result.

The third point considered is the question as to how far a temporary or permanent injury to the cytoplasm results in weakening the chlorophyll function. The effects of plasmolysis (Klebs, *Bot. Centr.*, 1887, 7, 166), of a constant electric current, heat, chloroform, nitric acid (1—2.5:10000) and ammonia were investigated. The results show that injury to the functions of chlorophyll by external influences is not exactly coincident with injury to the cytoplasm and the cell nucleus. The cytoplasm may lose its mobility without the elimination of oxygen being hindered. Constant electric currents seem to increase carbon assimilation in presence of light.

N. H. J. M.

Occurrence of Glutamine in Plants. By ERNST SCHULZE (*Landw. Versuchs.-Stat.*, 1898, 49, 442—446. Compare *ibid.*, 1896, 48, 33, and Abstr., 1896, ii, 572).—Glutamine probably takes the place of asparagine in the *Caryophyllaceæ* and perhaps also in the *Chenopodiaceæ*. It was previously mentioned that the seedlings in which glutamine was found were from seeds rich in fat. Seedlings of *Papaver somniferum*, *Tropæolum majus*, and *Pinus sylvestris* (the seeds of which are rich in fat) contained, however, considerable amounts of asparagine, but no glutamine.

The seedlings previously found to contain glutamine were etiolated. Glutamine occurs also in normal seedlings of *Ricinus communis*, *Sinapis alba* and *Picea excelsa*. The greatest amount of glutamine found in seedlings was only 2·5 per cent. in the dry matter, which is much less than the amount of asparagine found in leguminous seedlings; but it is supposed that, owing to the difficulties of separating glutamine, the plants contained at least twice as much as was actually obtained.

In the case of *Cruciferae*, glutamine occurs in the roots and tubers, but it is not to be supposed that plants which produce glutamine when germinating necessarily produce it at other periods when there is an accumulation of amides.

N. H. J. M.

Tyrosine in *Trifolium Pratense*. By N. A. ORLOFF (*Chem. Centr.*, 1897, i, 1234; from *Pharm. Zeit. Rüss.*, 36, 214).—The solution obtained by precipitating an aqueous extract of *Trifolium pratense* with lead acetate, and subsequently removing the excess of lead, produces with mercuric nitrate a precipitate which becomes red on standing or on being warmed; when this is decomposed by hydrogen sulphide, a substance is obtained which dissolves in ammonia, giving a solution that becomes turbid on adding acetic acid. These reactions probably indicate the presence of tyrosine.

W. A. D.

The Question as to how far Soil Analysis can indicate the Potash requirement of Soils. By OTTO LEMMERMANN (*Landw. Versuchs.-Stat.*, 1897, 49, 287—339).—Field experiments were made in which oats and wheat were grown on different soils of known composition, with and without kainite. Oats were also grown in pots in soil which had been extracted with 0·06, 0·25, 0·5, 1, and 5 per cent. hydrochloric acid, and in the same soil in its natural condition; mineral manures were added to some of the pots. The amounts of total produce and the lime, magnesia, potash, and phosphoric acid in the produce are given.

From the results of the experiments, it is concluded that, for rye and wheat, potash should be applied to soil which contains less than 0·2351 per cent. of potash soluble in 10 per cent. hydrochloric acid. Soil containing more than 0·2424 per cent. of potash does not require application of potash for oats.

N. H. J. M.

Composition of the Straw of Wheat, Oats, and Rye. By BALLAND (*Compt. rend.*, 1897, 125, 1120—1122).—Analyses of the straw of wheat, oats, and rye from different localities show that they all contain very little assimilable matter, and that, so far as chemical composition is concerned, they are practically identical. The percentage composition varied between the following limits:—Water, 9·20 to 14·50; nitrogenous matter, 1·01 to 3·22; fats, 0·92 to 1·60; extractive matters and saccharifiable cellulose, 39·43 to 48·04; non-saccharifiable cellulose, 32·90 to 39·15; ash, 2·86 to 6·94; and acidity, 0·044 to 0·118. These variations are mainly due to the fact that the composition of the leaves, the stem and the awns is not the same, and consequently the composition of the whole varies with the proportions of these organs. The composition of the stem is also different in its upper and lower portions. Analyses are given of the different parts of one sample of

oat-straw, one of rye-straw, and two of wheat-straw. Short straw with a high proportion of leaf should be selected for feeding purposes, and long straw is useful only for litter. C. H. B.

Food Value of Lucerne. By ACHILLE MÜNTZ and CHARLES A. GIRARD (*Ann. Agron.*, 1898, 24, 1—39).—A number of samples of lucerne, and samples of stems and leaves of lucerne were analysed, whilst the digestibility of fresh and dry lucerne, of the stems and leaves respectively, and of a mixture of lucerne and grass was determined by experiments with horses.

Green lucerne is not appreciably more digestible than lucerne which has been properly dried, the nitrogenous matter being in both cases equally utilised. Contrary to what would be expected, the cellulose becomes more digestible after the lucerne is dried, but this is probably owing to the fact that the horses eat the hay more slowly, and masticate it more thoroughly, than the green fodder. The other constituents, such as the pectic and gummy substances and organic salts, are more completely digested in green than in dry lucerne.

In the following summary, the percentage amounts of total and digestible constituents of lucerne and meadow hay are compared:—

	Nitrogenous matter.		N-free extract.		Crude cellulose.	
	Total.	Digestible.	Total.	Digestible.	Total.	Digestible.
Lucerne	10.90	7.85	39.71	26.29	27.54	10.77
Meadow hay ...	6.95	4.81	47.37	34.34	23.93	16.84

Lucerne contains, therefore, 3 per cent. more digestible nitrogenous, and 14 per cent. less non-nitrogenous, matter than meadow hay. It is suggested that lucerne may be considered better than hay for the production of force, whilst meadow hay would be the more suitable for fattening.

Comparing the produce from a given area of land, it is shown that lucerne produces 162 kilos. per hectare more digestible nitrogenous matter than a natural meadow, and that if the latter produces the more digestible non-nitrogenous matter, lucerne is the more valuable crop. Moreover, lucerne utilises a greater amount of atmospheric nitrogen than is the case with mixed herbage, and enriches the soil to a correspondingly greater extent. N. H. J. M.

Composition of Hemp. By FAUSTO SESTINI and GHERO, CATANI (*Landw. Versuchs-Stat.*, 1898, 49, 447—460).—Analyses are given of three samples of hemp stems in the natural state with the leaves and flowers, of the same number of samples of stems broken in the field, and of macerated stems. The results obtained with the natural stems of plants grown on the experiment field are as follows (per cent. in dry matter).

Organic matter.	Pure cellulose.	Ether extract.	Nitrogen.	Extractives.	Ash.
96.210	50.409	1.401	1.154	37.186	3.790

The pure ash contained (per cent.).

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ + Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
42.182	0.920	28.830	3.140	3.584	11.037	4.282	4.408	1.966

The results show that, with a normal yield of 100 cwt. of stems, the hemp crop is less exhausting than was indicated by former analyses. It is very important to break the stems on the land and to return the useless portions for manure.

N. H. J. M.

Amount of Pentosans in Different Feeding Materials, and the amounts remaining in the Foods after they have been subjected to Operations. By BERNHARD TOLLENS and HUBERT GLAUBITZ (*Chem. Centr.*, 1897, i, 613—614; from *J. Landw.*, 45, 97—111).—In examining the sulphuric acid and the caustic potash solutions used in determining crude fibre in brewers' grains, it was found that most of the pentosans were in the $1\frac{1}{4}$ per cent. sulphuric acid, a very small amount being found in the potash extract; some remained in the crude fibre. In meadow hay, 23.63 per cent. of the total pentosans was found in the crude fibre.

In the case of barley, malt, worts, and grains, three-fourths of the pentosans of the malt were found in the wort, the rest in the grains. Barley does not lose pentosans in germinating. In mashing, the dissolved pentosans of the malt are not all found in the wort, but in the beer also, as, even if they are partly converted into pentoses, they are not capable of alcoholic fermentation.

The determination of pentosans in food should be extended, as the digestible cellulose is equal in value to digestible starch.

N. H. J. M.

Effect of Different Potassium Salts on the Yield and Composition of Potatoes. By F. W. THEODOR PFEIFFER, E. FRANKE, OTTO LEMMERMANN, and H. SCHILLBACH (*Landw. Versuchs-Stat.*, 1897, 49, 349—385).—The experiments were made in zinc vessels containing 27 kilograms of fine sandy soil manured with blood meal, sodium nitrate, superphosphate, and caustic lime. There were six pots without potash, and thirty pots with various potassium salts.

Potassium chloride, in quantities up to 250 kilograms of potash per hectare, had the same effect as the sulphate, the chlorine having no injurious action on the growth of the potatoes. The same amount of potash, applied in the form of "crude salts" (rich in chlorides), instead of being beneficial, caused a slight decrease in the amount of starch produced. This is attributed to the presence of magnesium compounds, as well as other chlorides in the "crude salts."

A low percentage of chlorides in soil is possibly injurious to the growth of potatoes, and in some cases the direct application of chlorides may be beneficial.

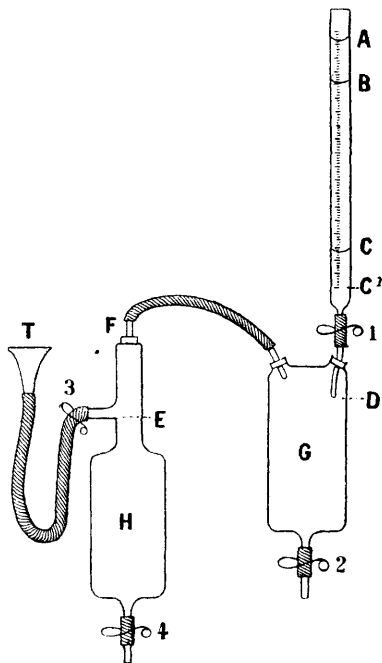
Unusually high production of starch is sometimes coincident with a very high percentage of chlorine in the tubers and above-ground growth, and it is suggested that, by cultivation under altered conditions, potatoes may gradually become accustomed to large amounts of chlorides, and may even require chlorides for producing heavy crops.

The experiments were made with one kind of potatoes (Reichskanzler), and the manures were applied in the spring immediately before sowing. These conditions are to be kept in view in considering the above conclusions.

N. H. J. M.

Analytical Chemistry.

Volumetric Estimation of Hydrofluoric Acid. By JULIUS ZELLNER (*Monatsh.*, 1897, 18, 749—755).—Hydrofluoric acid can be accurately estimated by standard potash, using phenolphthalein as indicator, by first adding an excess of the alkali, heating for a short time, and then titrating the hot solution with the acid. If cold solutions are employed, the error may be as great as 1 per cent. The acid solution is weighed in a small vulcanite bottle fitted with a fine-pointed vulcanite tube that can be closed with a pinch-cock. The apparatus for delivering a known volume of the acid for the final titration is as follows. The burette and the vessel *G* are of glass, whilst *H* and the funnel *T* are of vulcanite. *G* is filled with water to the level *D*, the pinchcock 1 is then closed, and 2 opened; *H* is filled to the level *E* with the acid by means of the funnel *T*, the cocks 2 and 3 are closed, and the burette filled with water. On opening the cock 1, an amount *a* of water flows into *G*, the level in the burette finally becoming stationary at *B*; the cock 4 is then opened as well as 1, and the requisite volume *x* of acid delivered, the level in the burette falling to *C*.



If *b* is the volume *BC*; *v* that of the vessel *G* together with the connecting tube *F* as far as *E*; *h*₁ the height *DB*, *h*₂ the height *C'D*, and *B_m* that of the water barometer; then the volume $x = \frac{(v-a)(h_1-h_2)}{B_m+h_2} + b$, if the temperature remains constant throughout the experiment.

It is pointed out that a solution of hydrofluoric acid of sp. gr. = 1.148 contains 41.1 per cent. HF, and not 35.35 as stated by Bineau; contamination with hydrofluosilicic acid greatly influences the density; the author's determinations were carried out using a vulcanite pyknometer.

W. A. D.

A Source of Error in Kjeldahl's Nitrogen Estimation.—By B. SJOLLEMA (*Chem. Zeit.*, 1897, 21, 740—741).—When using zinc to prevent bumping, a small amount of hydrogen is evolved, and this carries over a certain quantity of fixed alkali, which may cause an

error of 0.3 per cent. of nitrogen, or nearly 2 per cent. of nitrogenous matter.

The author has fixed to the distilling flask a specially constructed tube in which the gas is made to pass through a little water, and is consequently freed from any fixed alkali.

L. DE K.

Comparative Experiments on the Estimation of Phosphoric Acid.—By ALEXANDER CAMERON (*J. Soc. Chem. Ind.*, 1897, 16, 499—502).—When estimating the soluble phosphoric acid in superphosphate, the highest (and presumably most correct) result is obtained by treating the substance (2 grams) twice with 20—30 c.c. of cold water, and finishing the extraction with boiling water.

The most accurate method of estimation seems to be the molybdate-citrate method, in which, after first precipitating with molybdate, 0.1 gram of citric acid is added to the ammoniacal solution of the yellow precipitate before the addition of the magnesia mixture. Without this addition of citric acid, the results are unquestionably above the truth. A more rapid method, and one which does not involve the use of molybdate, is the "citrate" method. Although this method gives lower results, they can be made to agree with those of the molybdate-citrate method by adding 1/50 to the weight of the magnesium pyrophosphate obtained. A weighed quantity of citric acid is added (varying from 0.3 to 2 grams according to the class of phosphate and the amount of iron present, but kept as low as possible, since increase of citric acid leads to deficiency in the result). The liquid is boiled, excess of ammonia is added, then excess of acetic acid and ammonium oxalate. The calcium oxalate is filtered off and washed, the filtrate and washings not being allowed to exceed 200 c.c. The phosphoric acid is then thrown down with magnesia mixture in the usual manner. The precipitate should, however, be redissolved in hydrochloric acid and reprecipitated by ammonia after adding 0.1 gram of citric acid. Should the result be required rapidly, filtration may take place 10 minutes after adding the magnesia mixture (the liquid having been stirred continuously meanwhile), but in that case the weight of precipitate obtained should be increased by one milligram. When iron or aluminium is present, the calcium oxalate precipitate will contain a little of the phosphoric acid, but, on the other hand, the weight of the magnesia precipitate will be slightly increased.

M. J. S.

Estimation of Citrate-soluble Phosphoric Acid in Basic Slag.—By MAX PASSON (*Zeit. angew. Chem.*, 1897, 746. Compare Abstr., 1897, ii, 230).—Instead of Wagner's solution, which contains ammonium citrate and free citric acid, but which is difficult to prepare of the exact strength, the author recommends a solution made by dissolving 140 grams of citric acid and 30 grams of neutral potassium citrate and making up to a litre.

L. DE K.

Estimation of Citrate-soluble Phosphoric Acid in Basic Slag. By O. BÖTTCHER (*Chem. Zeit.*, 1897, 21, 783—785).—The author again recommends the direct precipitation with magnesium mixture instead of the troublesome molybdate method. Five grams

of the sample, which should be weighed in the same state as received, is introduced into a half-litre flask, which is then filled with Wagner's dilute ammonium citrate solution, and rotated for 30 minutes at the rate of 30—40 rotations per minute. The liquid is poured off from the deposit and at once passed through a filter.

Fifty c.c. of this filtrate is mixed as soon as possible, or, at all events, the same day, with 25 c.c. of Märcker's citrate solution and of his magnesium mixture, and agitated in a shaking apparatus for 30 minutes; the magnesium phosphate precipitate is then at once collected in a Gooch's crucible, washed, dried, ignited, and weighed.

L. DE K.

Detection of Arsenic and Antimony. By PONTUS H. CONRADSON (*J. Soc. Chem. Ind.*, 1897, 16, 518—519).—Hager's test for arsenic is sufficiently sensitive, but does not distinguish arsenic from antimony, and is useless if hydrogen sulphide is evolved with the hydrogen arsenide. The author employs four test papers, all of which are to be freshly prepared and used wet. Nos. 1, 2, 3 are prepared by placing drops of lead acetate, silver nitrate, and mercuric chloride solutions respectively in the middle of pieces of filter paper large enough to cover the test-tube. No. 4 is prepared by putting two drops of nitric acid (sp. gr. = 1.2) on the paper, and then two drops of potassium iodide solution (1:10) in the middle of the nitric acid spot. Either zinc or magnesium may be used to generate hydrogen from dilute sulphuric acid, and these materials must first be tested for sulphur, arsenic, and antimony by causing the evolved gas to act on papers 1 and 2 in succession for 15 minutes each. The substance is then added, and (with a slow evolution of gas) the papers are applied in the order of their numbers, and each exposed for 15 minutes. No. 2 is blackened by both arsenic and antimony; No. 3 acquires a lemon-yellow to orange-brown colour with arsenic, but a brownish-grey tint free from yellow with antimony; No. 4 becomes bright yellow to orange with antimony, but is not affected by arsenic or by pure hydrogen.

M. J. S.

Comparison of Rapid Methods for Estimating Carbonic Anhydride and Carbonic Oxide. By LOUIS M. DENNIS and C. G. EDGAR (*J. Amer. Chem. Soc.*, 1897, 19, 859—870). The authors have experimented with the apparatus devised by Honigsmann, Bunte, Orsat, Elliot, and Hempel, and have tabulated the results.

All these various apparatus work within 1 per cent., and with the exception of the first-named even within half a per cent. As regards speed and convenience none are equal to the Hempel apparatus. As in the Bunte and Elliot methods the aqueous potash can only be used once, these methods are very wasteful.

L. DE K.

Estimation of Potassium by Reduction of Potassium Platinochloride by means of Sodium Formate. By B. SJOLLEMA (*Chem. Zeit.*, 1897, 21, 739—740).—The author, after pointing out some defects in the commercial processes recently proposed for the estimation of potassium, now recommends that devised by Corenwinder and Contamine.

According to these authors, a solution containing 0.5 gram of the

material is acidified with hydrochloric acid, mixed with excess of platinic chloride, and evaporated on the water bath to a syrupy consistence; when cold, the residue is treated with a mixture of 9 parts of 95 per cent. alcohol and 1 part of ether, and after some hours the insoluble matter is collected on a filter and washed with the same mixture. It is then dissolved in boiling water and boiled with a solution of sodium formate; this reduces the platinum, which, after being washed first with acidified water and then with boiling water, is ignited and weighed. One atom of platinum corresponds with 2 atoms of potassium.

The author, however, prefers washing with 90 per cent. alcohol, instead of the mixture of alcohol and ether. L. DE K.

Analysis of Limestones. By KARL J. SUNDSTRÖM (*J. Soc. Chem. Ind.*, 1897, 16, 520).—An analysis embracing the estimation of the calcium and magnesium carbonates, silica and alumina and ferric oxide with sufficient accuracy for technical purposes, can be completed in 2—3 hours by the following scheme. One gram of substance is dissolved in 25 c.c. of normal hydrochloric acid, and the excess of acid estimated by normal alkali, using methyl-orange as indicator. A second gram is dissolved in acid, and the solution evaporated for silica. The filtrate from the silica is precipitated with ammonia for aluminium and iron, and the filtrate from this precipitate is mixed while boiling with a boiling solution of ammonium oxalate. After two or three minutes, the clear liquid can be decanted on to a filter. The precipitate is dissolved in hydrochloric acid and reprecipitated by ammonia, and weighed as calcium oxide after washing and igniting over a blast lamp. The magnesium is calculated from the difference between the acid neutralised and that required by the calcium found.

M. J. S.

Electrolytic Estimation of Cadmium. By DANIEL L. WALLACE and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1897, 19, 870—873).—The authors (compare Abstr., 1896, ii, 220) state that Heidenreich's failure to obtain correct results with Smith's electrolytic process is probably due to the use of a current of different strength. Two experiments are communicated, showing that 50 c.c. of a solution containing about 0.13 gram of cadmium oxide in the form of acetate deposited all the metal when electrolysed at a temperature of 50° with a current of 0.02 ampère for 37 sq. cm. of cathode surface, voltage 3.5, the time required for complete precipitation being about 4 hours.

The same amount of cadmium oxide dissolved in 2 c.c. of dilute sulphuric acid of sp. gr. = 1.09 and diluted to 30 c.c., deposited all the metal when electrolysed for 4½ hours at 50° with a current of 0.08 ampère for 37 sq. cm. cathode surface, voltage 2.5. The electrolytic process may also be employed for the separation of copper from cadmium if the liquid contains free nitric acid. A solution containing about 0.1 gram of cadmium, and the same amount of copper per 100 c.c., and also 2 c.c. of strong nitric acid, when heated to 50° and electrolysed with a current N.D.₁₀₀ = 0.10 ampère, voltage 2.5, deposits the copper completely in 3 hours, leaving all the cadmium in solution.

L. DE K.

Volumetric Estimation of Zinc. By EDWARD G. BALLARD (*J. Soc. Chem. Ind.*, 1897, 16, 399—400).—In titrating zinc solutions by sodium sulphide, the point at which an excess of sulphide is first present is very accurately ascertained by placing a drop of the mixture on a bright plate of silver (cleaned with chalk and ammonia), allowing it to remain for 10 or 20 seconds, and then wiping off with filter paper. One part of sodium sulphide in 20,000 of water will produce a stain. In cases where the amount of zinc is not known approximately, time may be saved by adding an excess of sulphide at once and titrating back with a zinc solution, watching the disappearance of the stain on silver. As zinc sulphide in presence of a large excess of ammonia blackens the silver, an excess of ammonia must be avoided as far as possible if working in the cold, but at 82° a much larger amount of ammonia may be present without disturbing the result.
M. J. S.

Estimation of Cerium in the Presence of the Rare Earths. By GEORG VON KNORRE (*Zeit. angew. Chem.*, 1897, 685—688; 717—725).—The mineral is boiled with sulphuric acid, and after diluting with water, the metals of the cerium group are precipitated with oxalic acid so as to free them from titanous and phosphoric acids; the oxalates are ignited, the residue dissolved in sulphuric acid, diluted, and a little persulphuric acid added to peroxidise the cerium; the excess of the reagent is then removed by boiling.

To the cold solution, an excess of a solution of hydrogen peroxide, previously standardised with potassium permanganate, is then added to reduce the metal to the cerous state. The undecomposed hydrogen peroxide is again titrated with permanganate, and the difference between the two titrations noted; if the permanganate solution has been standardised with metallic iron, 56 parts of the latter correspond with 140 parts of cerium.
L. DE K.

Methods of Analysis of Chrome Salts. By HENRY R. PROCTOR (*J. Soc. Chem. Ind.*, 1897, 16, 412—414).—Chromic acid is most conveniently estimated by causing it to liberate iodine from acidified potassium iodide. It is quite sufficient to mix the solution (containing not more than 0.01 gram of potassium dichromate or its equivalent) with 1 gram of potassium iodide and 5 c.c. of concentrated hydrochloric acid in a stoppered bottle, and allow a few minutes to elapse before titrating with thiosulphate. To ascertain the extent to which the chromic acid is combined with alkali, the solution may be directly titrated with standard alkali, using as indicator phenolphthalein to which normal chromates are neutral, whilst dichromates are acid. If chromic salts are also present, they are very readily oxidised to chromates by boiling with excess of permanganate after making alkaline with sodium hydroxide. The excess of permanganate is removed by cautious addition of alcohol to the boiling solution until the pink colour disappears.
M. J. S.

Separation of Tin, Arsenic, and Antimony. By WILLIAM DANCER (*J. Soc. Chem. Ind.*, 1897, 16, 403—405).—On treating the sulphides of the above metals with an excess of lime-water, the tin sulphide is converted into an insoluble, white substance, which, after

heating to about 80° , can be readily filtered and washed with boiling water; the antimony and arsenic sulphides dissolve, although the latter partially precipitates again in a short time. If arsenic is absent, the antimony can be recovered as sulphide by adding an excess of acid to the filtrate. If the arsenic does not amount to more than 5 or 6 per cent. of the tin, the whole of it will be present in the filtrate from the tin precipitate, and may be separated from the antimony by adding ammonia (5 c.c. to each 100 c.c. of solution), heating to near boiling, and adding acetic acid drop by drop until a small, permanent precipitate is formed. A short boiling then precipitates the antimony as sulphide, and after filtering hot, the arsenic is obtained by adding hydrochloric acid to the filtrate. If, however, the arsenic exceeds the above proportion, the tin precipitate must be dissolved in yellow ammonium sulphide, the solution diluted and boiled, lime added gradually, and the boiling continued until the ammonia is nearly all expelled. The liquid is then cooled and filtered, and the arsenic precipitated from the filtrate by hydrochloric acid. The tin precipitate which contains calcium is ignited and boiled with dilute nitric acid to remove calcium. If the arsenic is in excess, repetitions of the processes may be necessary.

M. J. S.

Volumetric Estimation of Antimony. By HENRI E. CAUSSE (*Compt. rend.*, 1897, 125, 1100—1103).—When antimonious acid, either free or in combination, is brought into contact with iodic acid, decomposition takes place in accordance with the equation $5\text{Sb}_2\text{O}_3 + 2\text{I}_2\text{O}_5 = 5\text{Sb}_2\text{O}_5 + 2\text{I}_2$, and the liberated iodine can be estimated in the usual way with thiosulphate solution. The iodic acid solution is prepared by dissolving 50 grams of the acid in 250 c.c. of water. The antimony compound, containing from 0.5 to 0.6 gram of antimonious anhydride, is placed in a flask connected with a set of condensing bulbs (Mohr or Fresenius' apparatus) and mixed with 20 to 25 c.c. of the iodic acid solution. Ten c.c. of a 20 per cent. solution of potassium iodide is placed in the condenser, and the liquid in the flask is boiled until all the iodine has been expelled. The iodine solution in the condenser is diluted with water and titrated in the usual way.

Antimony can be determined in this way in any of its compounds. The metal is precipitated as sulphide, washed, dissolved in hydrochloric acid, and after expelling all the hydrogen sulphide, precipitated with sodium carbonate. The precipitate, when washed, may be heated directly with the iodic acid solution, or may be first dissolved in tartaric acid, or sodium hydrogen tartrate, neither of which has any action on iodic acid. All acids such as the halogen hydracids, sulphurous acid, or hydrogen sulphide, that interact with iodic acid, must, of course, be absent from the liquid.

C. H. B.

Analysis of Bearing Metal Alloys; New Volumetric Method for Estimating Copper. By W. E. GARRIGUES (*J. Amer. Chem. Soc.*, 1897, 19, 934—948).—The most interesting point in this elaborate article is a new method of estimating copper.

The solution, which must contain sulphuric acid only, is mixed with excess of sulphurous acid and precipitated by means of ammonium

thiocyanate, precipitation being promoted by gently heating; after the precipitate has been washed until no longer acid, the filter and its contents are put back into the beaker, boiled with a measured excess of standard alkali, and, when cold, diluted to a known volume, say 200 c.c. Half the liquid is then passed through a dry filter and the free alkali is estimated with standard acid, using methyl-orange as indicator. One equivalent of sodium hydroxide removed is equivalent to one of copper.

The following is a summary of the process for a complete analysis. Antimony is estimated by Mohr's method: titration with iodine in alkaline solution, the antimony being first reduced by Gooch and Gruener's method (*Abstr.*, 1892, ii, 242). Lead is estimated as sulphate, being collected on a Gooch crucible, dried (not ignited), and weighed. Tin is weighed as oxide, or, in presence of antimony, is determined by difference in weight. Arsenic is determined by Lundin's distillation process, and phosphorus is weighed as magnesium pyrophosphate.

L. DE K.

Colorimetric Estimation of Ammonia, Nitrous Acid, and Iron in Waters. By F. JOSEF KÖNIG (*Chem. Zeit.*, 1897, 21, 599—601).—The author tests for ammonia by adding to 300 c.c. of the water 2 c.c. of a soda solution made by dissolving 2.7 grams of pure crystallised sodium carbonate in 5 c.c. of water, and adding 1 gram of sodium hydroxide dissolved in 2 c.c. of water. The clear liquid is then poured off and tested with Nessler's solution. Nitrites are tested for by first clarifying the water, if necessary, with the soda solution after having previously added a little alum; the filtrate is then treated with zinc iodide, starch solution, and dilute sulphuric acid. Iron is found by boiling 500 c.c. of the sample with 1 c.c. of hydrochloric acid and a crystal of potassium chlorate, cooling, and adding a solution of ammonium thiocyanate. If a quantitative estimation be desired, comparative trials are made with liquids containing known quantities of either ammonium chloride, silver nitrite, or iron-alum.

To avoid using standard solutions, the author instructed an artist to copy the tints produced in 100 c.c. of the standard solution by the reagents, and has had these tints reproduced by lithography. Six graded slips, whose length and breadth are equal to the height and diameter of a Nesslerising tube filled to the 100 c.c. mark, are arranged as the faces of a hexagonal prism on a stand, so that they may be rotated round its vertical axis and successively compared with a Nessler glass containing the sample to be tested, which is supported on an arm of the same stand. The slips are marked with the quantity of the impurity in 100 c.c. to which they correspond, but on account of personal equation, it is advisable that each operator should himself prepare his standard solutions and make the necessary corrections. After adding the reagent, the liquid should, if necessary, be diluted so as to make its colour correspond with one of the tints.

L. DE K.

Estimation of Mineral Matter in Rubber Goods. By LEONARD DE KONINGH (*J. Amer. Chem. Soc.*, 1897, 19, 952—956).—The ash of a rubber does not always represent the true amount of mineral matter,

as the latter often diminishes seriously in weight during ignition. The author, therefore, proposes to first extract the bulk of the mineral matter with hydrochloric acid; for this purpose, 5 grams of the finely divided (rasped) sample is treated with 50 c.c. of strong hydrochloric acid, first in the cold and subsequently at a temperature of 70° , for an hour; 50 c.c. of water is then added and the insoluble matter, after being collected on a filter and washed with boiling water until no longer acid, is dried finally for 3 hours at 105° , and weighed. The little inorganic matter still remaining in it is found by ignition.

L. DE K.

Analysis of Asphaltum. By STEPHEN F. and H. E. PECKHAM (*J. Soc. Chem. Ind.*, 1897, 16, 424—427).—The authors criticise adversely the paper of H. Endemann (this vol., ii, 199), mainly on the ground that he omitted to notice the sulphur which is contained in crude bitumen, and which they regard, on grounds for which they produce no evidence, as existing in the form of an organic thio-salt of iron and as an essential part of the bitumen.

ENDEMANN, in reply, states that the substances which he analysed, and for which he gave formulæ, contained only traces of sulphur, and he attributes the hydrogen sulphide, which is produced in large quantity when crude bitumen is heated, to a reaction between iron pyrites and the hydrocarbons of the paraffin series which are always present in the substance.

M. J. S.

Estimation of Glycerol in Wine. By CARL BOETTINGER (*Chem. Zeit.*, 1897, 21, 658—659).—The glycerol obtained from wines by the conventional process being still strongly contaminated with other constituents of the wine, the author has devised a method to ascertain the true amount of glycerol; this is based on the fact that glycerol, when heated with acetic anhydride, yields triacetin which may be separated by means of ether.

About 1 gram of potassium pyrosulphate is introduced into a stoppered flask of about 7.5 c.c. capacity and after the whole has been weighed, about 1 gram of the crude glycerol is introduced and its exact weight ascertained by re-weighing; 1—1.5 c.c. of acetic anhydride is now added, and the closed flask is then placed for 2 hours in the water oven. When cold, the mass is moistened with a few drops of absolute alcohol and then repeatedly extracted with ether, the ethereal solution evaporated in a tared beaker, and the residue heated for 4 hours at a temperature of exactly 105° ; when cold, the residue is quickly weighed. It consists of almost pure triacetin, 151.4 parts of which correspond with 100 parts of glycerol.

L. DE K.

Estimation of Cane-sugar in Prepared Cocoa. By LEONARD DE KONINGH (*Zeit. angew. Chem.*, 1897, 713).—16.35 grams of the sample is introduced into 100 c.c. of water, and after thoroughly stirring for about 10 minutes, the solution is filtered; 50 c.c. of the filtrate is then mixed with 5 c.c. of *liquor plumbi*, B.P., and the filtrate examined in a Dubosq's polariscope, using a 22 cm. tube.

Suppose the polarisation is 47° , this is provisionally called the percentage of sugar in the sample. 16.35 grams of cane-sugar, when

dissolved in water, causes an increase of 10.2 c.c. of liquid; the sample containing 47 per cent., or $16.35 \times 0.47 = 7.68$ grams of sugar, will have caused the liquid to increase by 4.8 c.c. The true amount of cane-sugar is therefore represented by $47 \times 104.8/100$. This way of calculating is, of course, not strictly accurate, but it meets practical requirements. The author has never met with a pure cocoa which, when treated with a properly prepared lead solution, showed any polarisation.

L. DE K.

Characteristic Colour Reaction of Acetaldehyde. By LOUIS SIMON (*Compt. rend.*, 1897, 125, 1105—1107).—When a dilute aqueous solution of acetaldehyde is mixed with a small quantity of a solution of trimethylamine, and a few drops of a very dilute solution of sodium nitroprusside is added, an intense blue coloration gradually develops, which is recognisable even with solutions that contain 1 part of acetaldehyde in 25,000. This reaction is much more sensitive than Legal's reaction, or the reaction with magenta and sulphurous acid, but the coloration is somewhat fugitive, and disappears after about 15 minutes in very dilute solutions.

This reaction is characteristic of acetaldehyde; it is not given by paraldehyde, chloral, formaldehyde, propaldehyde, butaldehyde, benzaldehyde, acetone, methyl ethyl ketone, acetophenone, bromacetophenone, benzophenone, phenylglyoxylic acid, glucose, or camphor. It can, therefore, be used, for example, for the detection of aldehyde in ether, alcohol, or acetone. The last compound gives a red coloration with the reagent, but this is completely masked by the blue colour when the proportion of aldehyde reaches 1 part in 1000.

Ammonia and amines give a blue coloration with pyruvic acid in presence of nitroprussides (this vol., i, 64), but ammonia and a nitroprusside give no coloration with aldehyde. Ammonia, on the contrary, destroys the colour produced by trimethylamine, and thus constitutes a striking difference between the amine and ammonia.

Potassium hydroxide, when added to the blue solution, displaces the amine, and the blue coloration gives place to the red colour of Legal's reaction. Acetic acid changes the blue colour to violet, and then destroys it.

C. H. B.

Estimation of the Acidity of Urine. By H. JOULIE (*Compt. rend.*, 1897, 125, 1129—1130).—The acidity of urine is best estimated by means of a solution prepared by agitating 10 grams of calcium oxide for some time with a solution of 20 grams of cane-sugar in 1000 c.c. of water, and diluting the clear liquid until it is decinormal. The point of neutralisation is best indicated by the production of a permanent turbidity due to the precipitation of calcium phosphate. The quantity of urine taken for the estimation should be 20 c.c., or such greater quantity as may require not less than 5 c.c. of the calcium oxide solution to neutralise it. If necessary, the urine must be previously filtered.

Since the proportion of water in urine is very variable, whilst the quantity of solid matter is somewhat constant, it is important to ascertain, not the acidity per litre, but the acidity per given quantity of solid matter. For this purpose, the acidity per litre is multiplied by the fraction $100/D - 1000$, in which D is the specific gravity at the

temperature at which the urine was measured off for the acidity determination. The value thus obtained is characteristic of the temperament of the individual in normal health, or of his pathologic condition during illness.

C. H. B.

Reaction of Urine. By L. DE JAGER (*Zeit. physiol. Chem.*, 1898, 24, 303—321).—Various errors are considered in the methods adopted by Lieblein and by Freund in the estimation of the acidity of urine, and numerous experiments with various solutions of phosphates were made, but it is pointed out that urine is a complex solution, and contains ammonia, and also urates, which affect the reaction. When barium chloride is added, barium sulphate, acid barium phosphate, and barium urate are formed, but some uric acid remains in solution.

W. D. H.

Hehner's Bromine Thermal Test for Oils. By LEONARD ARCHBUTT (*J. Soc. Chem. Ind.*, 1897, 16, 309—311, and 411.) The author having obtained considerable experience in the application of this method (this vol., ii, 197), confirms its value as a rapid process for ascertaining the iodine absorption of an oil, and describes in detail his mode of conducting it. The oil having been weighed into the vacuum-jacketed tube and dissolved in 10 c.c. of methylated chloroform, is brought to exactly the same temperature as the bromine, and 1 c.c. of the latter (measured with a pipette furnished with a guard tube of soda lime) is immediately added. The mixture is stirred with the thermometer, and the maximum temperature, which is reached in about 15 seconds, is read off. It is unimportant whether the bromine is anhydrous or saturated with water, and the rise of temperature seems to be independent of variations in the initial temperature. Although 1 gram of oil is usually employed, it is well to use 2 grams of fats like tallow, which develop comparatively little heat, and to halve the result. Of linseed oil, 0.5 gram is sufficient, as the reaction is very violent. Each oil requires, however, a special factor for the calculation of the iodine number, and as these factors differ with different instruments, they must be ascertained by each operator for himself.

M. J. S.

Analysis of Fats: The Acetyl Value. By JULIUS LEWKOWITSCH (*J. Soc. Chem. Ind.*, 1897, 16, 503—506).—The author has previously shown (*Proc.*, 1890, 72, 91; *Abstr.*, 1891, 511) that, on heating the higher fatty acids with excess of acetic anhydride, the anhydrides of the fatty acids are obtained. When these are dissolved in alcohol and treated with potash, partial but incomplete hydrolysis occurs, less potash being neutralised than the theoretical amount for the fatty acid in question. The method employed by Benedikt and Ulzer for ascertaining the amount of hydroxylated fatty acid in a mixture is invalidated by the occurrence of these reactions. It is therefore proposed to ascertain the "acetyl value" of a fat by the direct estimation of the acetic acid obtained on saponifying the acetylated fat. The glycerides of hydroxylated fatty acids are acetylated by boiling for 2 hours with an equal volume of acetic anhydride. The product is freed from the excess of acetic anhydride by boiling repeatedly with water until the water no longer becomes acid. The oily layer is then

freed from water, and filtered through paper in an oven. The operation can be made quantitative by washing on a weighed filter, in which case the increase in weight is a rough measure of the amount of acetylation which has taken place. A weighed quantity of the product (2—4 grams) is then saponified with alcoholic potash in the usual way, the alcohol is evaporated, and the soap dissolved in water; two methods are then available for ascertaining the amount of acetate produced. (1) The "*distillation process*." An excess of sulphuric acid is added and the acetic acid distilled with water, or by blowing steam through the mixture. It is sufficient to distil over 500—700 c.c. The distillate is filtered and titrated with alkali. (2) The "*filtration process*." A quantity of standard sulphuric acid is added exactly corresponding with the amount of alcoholic potash used, and the mixture is gently warmed, when the fatty acids collect as an oily layer; this is filtered off and washed with boiling water, and the filtrate is titrated with alkali. Both processes give the same result, but the second is the more convenient. The "acetyl value of a fat" is therefore definable as the number of milligrams of potassium hydroxide required for neutralising the acetic acid obtained on saponifying 1 gram of the acetylated fat. The results obtained with 14 different fats are given, and these differ considerably from those published by Benedikt and Ulzer.

Should free alcohols be present, these will of course be acetylated. In this case, the alcohols must be separated, and their amount and acetyl value estimated and deducted before employing the results for the calculation of the hydroxylated fatty acids present. The case of fats containing volatile fatty acids (Reichert values) will be dealt with subsequently.

M. J. S.

Estimation of Fat. By OSVALDO POLIMANTI (*Pflüger's Archiv*, 1898, 70, 366).—The use of Soxhlet's apparatus alone will not extract all the fat from flesh. If, however, 2 grams of powdered flesh is shaken for 6 hours with 200 c.c. of ether, 2 c.c. of mercury being also added, and the fat then estimated in an aliquot part of the extract, the same figure is obtained as by extraction in a Soxhlet's apparatus for 48 hours after artificial gastric digestion as in the Pflüger-Dormeyer method.

W. D. H.

Estimation of Undigested Fat and Casein in Fæces. By HERMAN POOLE (*J. Amer. Chem. Soc.*, 1897, 19, 877—881).—The material is first extracted with ether, the ethereal solution evaporated to dryness at 100°, and the residue saponified by alcoholic potash; water is then added, and after the alcohol has been expelled by boiling, the liquid is filtered and the cholesterol removed by shaking in a separating funnel twice in succession with an equal bulk of ether. The aqueous liquid now contains the fatty acids, which are liberated and collected in the usual way, and calculated to, say, butter-fat.

The residue from the treatment with ether, after being extracted successively with water and with alcohol, is dried, and digested overnight in a mixture of 30 parts of hydrochloric acid and 70 parts of water at 50°; this dissolves the casein, leaving the epithelium *débris* and soapy matters. When cold, the liquid is filtered, evaporated, and the casein estimated by the Kjeldahl method.

L. DE K.

Detection of Veratrine. By G. LAVES (*Zeit. anal. Chem.*, 1898, **37**, 61; from *Pharm. Zeit.*, **37**, 338).—Three or four drops of a 1 per cent. solution of furfuraldehyde is mixed with 1 c.c. of concentrated sulphuric acid and 3–5 drops of the mixture is brought in contact with the solution to be tested. At the point of contact, a blue or bluish-violet colour appears, and this changes to green as it extends into the reagent. On mixing, the whole becomes deep green, which changes on warming to blue and violet.

M. J. S.

Estimation of Resin in Hops. By LAWRENCE BRIANT and CHARLES S. MEACHAM (*J. Fed. Inst. Brew.*, 1897, **3**, 233–236).—About 4 grams of the sample are placed in a Soxhlet apparatus and extracted for 24 hours with light petroleum boiling at about 50°. The soft resins so extracted are dried in the steam oven and weighed. The extraction of the residue in the Soxhlet apparatus is then continued for 12 hours more with ordinary ether, and the hard resins obtained in this way are dried and weighed in the same manner.

A. C. C.

Estimation of Tannin. By LEOPOLD MASCHKE (*Zeit. anal. Chem.*, 1898, **37**, 51–52; from *Ding. poly. J.*, **302**, 46).—The usual way of correcting the crude result obtained by estimating the solid residue before and after treatment with hide powder, is to make a blank experiment with the hide powder under similar conditions, and to ascertain the amount of soluble matter thus obtained; the author points out, however, that these soluble constituents of the hide powder are for the most part precipitated by tanning materials, and that the correction is, therefore, too large. Especially is this the case with inferior qualities of hide powder.

The Löwenthal-Schröder method is affected in the same way.

M. J. S.

Detection of Indican in Urine. By A. LOUBIOU (*Chem. Centr.*, 1897, **i**, 620; from *Rev. Chim. anal. appl.*, **5**, 61–62).—One to two c.c. of the urine is mixed in a test-tube with an equal volume of chloroform and 1 c.c. of 5–10 per cent. solution of hydrogen peroxide; 2 volumes of strong hydrochloric acid is next added, and the mixture gently heated, turning the tube meanwhile at least twenty times round its axis. On standing, it will be noticed that the layer of chloroform is blue if indican is present. The test is very sensitive and may, perhaps, form the basis of a colorimetric estimation of indican.

L. DE K.

Detection of Peptone (Albumoses) in Urine and Preparation of Urobilin. By ERNST L. SALKOWSKI (*Chem. Centr.*, 1897, **i**, 1133–1134; from *Berl. klin. Woch.*, **34**, 353–357).—The author finds that the test for peptone or albumoses in urine, previously described by him (*Abstr.*, 1894, **ii**, 372), which consists essentially in acidifying the urine with a few drops of hydrochloric acid, precipitating with phosphotungstic acid, dissolving the precipitate in dilute sodium hydroxide solution, and applying the biuret reaction, may be vitiated by the presence of urobilin, as the latter gives this reaction and is mechanically carried down by the phosphotungstic acid precipitate.

Some urines, however, and even those which show absorption bands plainly, do not give the biuret reaction, but in such cases, after precipitating with phosphotungstic acid and applying this test, absorption bands may be detected. Since lead acetate in acid or neutral solution not only precipitates urobilin but also more or less albumose, in order to test for the latter in presence of the former, the author prefers to treat the urine directly with phosphotungstic acid and then to employ only 10—15 c.c. for the biuret test, so as to minimise the effect of the colouring matters. By using amyl alcohol or charcoal to eliminate the urobilin, albumoses may also be removed; when charcoal is employed, the operation should be carried out as quickly as possible.

The author has prepared urobilin from urine by Jaffé's method, but obtained a very poor yield. Urobilin forms a lustrous, reddish-brown mass which is green by reflected light; unlike Jaffé's preparation, it is brittle and insoluble in ether. When a solution of urobilin in ethyl acetate is shaken with water, the latter becomes strongly yellow and absorbs the whole blue and violet portion of the spectrum. When sodium hydroxide solution is added, this absorption is almost destroyed, but, on adding zinc chloride, the absorption bands are restored and the solution acquires a strong green fluorescence; by means of this reaction, as little as one-seventh of a milligram in 5 c.c. of solution may be detected. When copper sulphate is added to an alkaline 0.003 per cent. solution of urobilin, the mixture becomes red and shows ill-defined absorption bands. Urine containing only 0.003 per cent. of urobilin gives only a very faint biuret reaction, but with ammonia and zinc chloride shows the characteristic green fluorescence. Faeces are rich in urobilin.

E. W. W.

A Simple Albuminometer. By E. RIEGLER (*Chem. Centr.*, 1897, i, 558; from *Apoth. Zeit.*, 12, 89).—A mixture of equal parts of citric acid and asapol is measured in a spoon belonging to the apparatus and introduced into a graduated tube, which is then filled up to a certain mark with the urine to be examined. After shaking and then leaving it for 24 hours, the volume of the deposit is read off. Each division represents 1 gram of albumin in a litre of urine (compare *Abstr.*, 1897, ii, 84).

L. DE K.

Estimation of Proteids by Chlorine. By SAMUEL RIDEAL and C. G. STEWART (*Analyst*, 22, 228—233).—The authors' object was to obtain a trustworthy process for the estimation of gelatin in meat extracts, and they find that it can be completely precipitated from a dilute solution by means of a current of chlorine. The weight of the precipitate, after being dried in a vacuum over sulphuric acid, is to the gelatin taken as 1:0.78. Meat bases are not precipitated by chlorine.

Unfortunately, any albumins, or albumoses, are also precipitated by chlorine (a fact already noted by Mulder, who called the precipitated substance "proteinchlorous acid"), but it is found that the weight of the chlorine precipitate from any proteid (other than peptone), when multiplied by 0.78, gives results which seem to be in close accord with the known amount.

L. DE K.

Improved Method of Estimating Proteids and Gelatinous Substances. By ALFRED H. ALLEN and A. B. SEARLE (*Analyst*, 22, 258—263).—The authors have substituted bromine water for chlorine in the separation of proteids from meat bases (see preceding abstract).

Both albumoses and gelatin are precipitated and may be readily collected; after washing slightly with dilute bromine water, the precipitate is treated by Kjeldahl's process, and from the nitrogen thus found the proteids are calculated. Experiments are given showing that the precipitation by bromine is complete. The solution should contain sufficient hydrochloric acid to be distinctly acid to litmus paper. L. DE K.

Detection of Gelatin in Cream. By ALFRED W. STOKES (*Analyst*, 22, 320—321).—Mercury is dissolved (in the cold) in twice its weight of nitric acid of sp. gr. = 1.42, and then diluted with water to 25 times its bulk. To 10 c.c. of this solution, 10 c.c. of the sample of cream and 20 c.c. of water are added. After shaking, and waiting for 5 minutes, the mixture is filtered; but if much gelatin is present, a clear filtrate cannot be obtained. The filtrate is tested for gelatin by adding an equal volume of a cold saturated aqueous solution of picric acid, which will give a yellow precipitate if gelatin is present. Picric acid gives a precipitate with 1 part of gelatin in 10,000 of water. L. DE K.

Urobilin. By GEORGES DENIGÈS (*Chem. Centr.*, 1897, i, 1128—1129. See this vol., i, 343).

Modification of the Method for the Detection of Urobilin in Urine. By G. LEO (*Chem. Centr.*, 1897, i, 440; from *Boll. Chim. Farm.*, 36, 69—70).—The precipitate obtained on adding basic lead acetate to 150—200 c.c. of the sample, after being washed with water until practically free from soluble lead salts, and then with 8—10 c.c. of absolute alcohol, is treated with 10—12 c.c. of alcoholic ammonia (10 vols. of alcohol and 2 vols. of aqueous ammonia), the liquid being poured again and again through the filter. The ammoniacal solution is then concentrated on the water bath and tested for urobilin with ammoniacal zinc chloride, which gives a fluorescent, green solution; sulphuric acid changes this to a reddish colour if care is taken to avoid any rise of temperature. The colouring matter may be extracted by agitating the liquid with amyl alcohol. L. DE K.

Detection of Horseflesh in Sausages. By HERMANN BREMER (*Chem. Centr.*, 1897, i, 520—521; from *Forsch. Ber. Lebensm.*, 4, 1—8).—The sample, freed from large pieces of pork, is boiled with water, which is then poured off, together with any fat floating on it, and the residue dried for 12 hours at 100°. It is then powdered, exhausted with light petroleum, the latter evaporated, and the residue consisting of "intermuscular fat" is weighed. This fat should give an iodine figure of 65, and its liquid fatty acids isolated by the zinc-ether process a figure of 95. If these figures are largely exceeded, horseflesh is present. L. DE K.

General and Physical Chemistry.

Connection between Volume Change and Specific Rotation of Active Substances. By RICHARD PRIBRAM and CARL GLÜCKSMANN (*Monatsh.*, 1897, 18, 510—526. Compare Abstr., 1897, ii, 534.)—Solutions of rubidium tartrate show a maximum contraction in volume at a point corresponding with about 5 per cent. of the dissolved salt. A change in the direction of the specific rotation curve also occurs at about the same point with these solutions. These changes in specific rotation show that the values calculated by extrapolation for solutions of infinite dilution on the one hand, and for the anhydrous compounds on the other, must have a very uncertain value. Rimbach (Abstr., 1895, ii, 301) examined rubidium tartrate solutions, but failed to note the change recorded above, and hence his calculation of $[\alpha]_D$ cannot be regarded as correct.

For the change in specific rotation with change in concentration, the authors propose the term "allaxis." Where the change is a regular one and the curve is rectilinear, it is termed "isallactic"; when the curve is not rectilinear, "heterallactic." H. C.

Spectrum of Cadmium in a Vacuum. By MAURICE HAMY. (*Compt. rend.*, 1898, 126, 231—234).—The wave-lengths of the rays emitted by cadmium in a vacuum tube were determined by Michelson's interference method and calculated from the wave-length, already known, of the red ray 0.6438472. The relative intensities of the rays and their wave-lengths are as follows.

Intensity	1	4	3	3	2
λ	0.6438472	0.6325161	0.5378128	0.5337477	0.5154655
Intensity	1	1	2	4	5
λ	0.5085832	0.4799919	0.4678153	0.4662345	0.4415702

The sixth and seventh rays are complex, but all the others are very simple, with the exception of the eighth, which is somewhat complex. The presence of air in the tube simplifies the complex rays and causes some of the simple rays, notably the third, fourth, and fifth, to disappear altogether. C. H. B.

Electrical Resistance of Crystallised Silicon. By FERNAND LE ROY (*Compt. rend.*, 1898, 126, 244—246).—The author suggests the substitution of resistances of crystallised silicon in place of metallic resistances when electrical heating is required. Its resistance, specific heat, and emissive power are all high. It is easy to prepare sticks of pure agglomerated silicon 10 cm. long and 40 sq. mm. in sectional area, with a resistance which varies with the physical condition of the silicon, but may be as much as 200 ohms, whilst the resistance of similar rods of carbon is only 0.15 ohm, and of German silver only 0.00085 ohm. It follows that, for a given resistance, the rods of carbon must be much smaller than those of silicon, and the

rods of German silver very much smaller still. The resistance of silicon diminishes as the temperature rises, and at 800° is only about 0.6 of its value at the ordinary temperature. C. H. B.

Electrical Conductivity of Dilute Solutions at Various Temperatures up to 100° . By R. SCHALLER (*Zeit. physikal. Chem.*, 1898, 25, 497—524).—In order to avoid the action of water on glass at high temperatures, a platinum vessel was employed, but it was found that, in the case of acids and neutral salts, vessels made of Jena glass might be used. The measurements at 25° before and after heating were found to differ by about 3 per cent., and this difference was ascribed to changes in the electrodes, as it became considerably less after the electrodes had been used frequently at the high temperatures. The conductivity of the water employed rose from about 1×10^{-6} at 25° to about $2.6\text{--}2.8 \times 10^{-6}$ at 99° . An approximately equal temperature coefficient was obtained with solutions of potassium chloride, sodium chloride, potassium nitrate, and sodium nitrate, being about $2000\text{--}2300 \times 10^{-6}$ and increasing slightly with the temperature. For hydrochloric acid, the coefficient is much smaller, $1200\text{--}1400 \times 10^{-5}$, and decreases with rise of temperature. The migration velocities of the various ions are calculated for temperatures up to 100° , the assumption being made that the velocities of the potassium and chlorine ions are equal at all temperatures. The sodium salts of cinnamic, orthotoluic, paratoluic, benzoic, orthoiodobenzoic, metiodobenzoic, orthonitrobenzoic, metanitrobenzoic, parachlorobenzoic, and anisic acids were also examined. The molecular conductivity was found to increase with rise of temperature, but at a diminishing rate, in some cases reaching a maximum and then decreasing; the degree of dissociation however, as well as the heat of dissociation, which is calculated from the temperature coefficient, was found in each case to decrease with rise of temperature, the heat of dissociation frequently changing at the higher temperatures from a positive to a negative value. L. M. J.

Dissociation of Electrolytes as Measured by the Boiling Point Method. By HARRY C. JONES and STEPHEN H. KING (*Amer. Chem. J.*, 1897, 19, 753—756).—The Beckmann boiling point apparatus in its improved form has been applied to the measurement of the electrolytic dissociation of solutions of potassium iodide and sodium acetate in ethylic alcohol. The dissociation of potassium iodide in alcohol is between one-third and one-fourth of that in water at the same dilution. This is just about the same ratio as exists between the dielectric constant of these two solvents. The dissociation found for sodium acetate is very low, but the authors are inclined to attribute this to slight impurity in the salt. H. C.

Electric Furnaces. By GIN and LELEUX (*Compt. rend.*, 1898, 126, 236—238).—The characteristic fall of potential of an arc striking across a given medium is due simply to the resistance of the mass of gas which lies between the electrodes resulting from the volatilisation of the material of the electrodes or of the substances subjected to the action of the arc. If this mass of gas is regarded as a cylinder with a

sectional area equal to that of the electrodes, and if this cylinder is assumed to be surrounded by a perfect thermal screen, it can be shown that the temperature of the arc would increase as the square of the density of the current and the ratio of the resistivity to the specific heat per unit volume of the atmosphere of the arc, the two latter factors being themselves variable with the temperature.

When the arc is allowed to pass through a mixture such as that used in the preparation of calcium carbide, the arc forms round itself a sort of pocket, at the upper pole of which is a small crater through which carbonic oxide and the vapours of calcium oxide, calcium, and carbon escape. The volume of this cavity increases up to the point at which the heat liberated by the arc is in equilibrium with the loss of heat to the surrounding medium. After cooling, it is found that the interior of the pocket is lined with a brilliant layer of vesicular graphite, behind which is a concentric layer of crystallised calcium carbide, and behind this a layer of unaltered material. This result can be explained by assuming either that at the temperature of the arc the calcium carbide dissociated, or that part of the calcium oxide volatilised so rapidly that it escaped reduction, and an excess of carbon was left. Direct experiment shows, however, that with a sufficiently intense arc, calcium carbide is dissociated at a temperature below that at which carbon volatilises. The tension of the arc varies with the surrounding atmosphere; for example, with calcium carbide mixture when the stationary temperature is reached the tension is from 18 to 20 volts, the electrodes being 10 cm. apart, whilst with a mixture of carbon and manganese oxide the tension is only 10 volts, and the pocket formed is much larger.

C. H. B.

Conditions required for attaining Maximum Accuracy in the Determination of Specific Heat by the Method of Mixtures. By F. L. O. WADSWORTH (*Amer. J. Sci.*, 1897, [iv], 4, 265—282).—From a mathematical discussion of the conditions required for attaining the maximum degree of accuracy in specific heat determinations by the method of mixtures, it appears that the greatest possible care should be taken in reading temperatures, since the errors of these readings are much greater than any others likely to be committed. The author advises, therefore, the use of a small amount of water in the calorimeter and a small calorimeter, a large mass of metal having a maximum surface for a given weight, and as high an initial temperature as can be conveniently attained. The calorimeter should be surrounded by a water jacket maintained at a constant temperature, higher than the initial temperature of the water in the calorimeter.

H. C.

Preliminary Thermochemical Study of Iron and Steel. By EDWARD D. CAMPBELL and FIRMAN THOMPSON (*J. Amer. Chem. Soc.*, 1897, 19, 754—766).—The authors give measurements of the heats of solution of samples of iron and steel in a slightly acid solution of potassium copper chloride. The chemical composition and heat evolved, on dissolving 1 gram of the metal examined, are given in each case. Thirty-five different samples of iron and steel were

treated in this way, and the following points seem to be indicated by the results obtained.

In annealed metal, owing to the heat of formation of compounds of iron with carbon, the heat of solution diminishes as the percentage of carbon increases, until after the saturation point (eight-tenths to nine-tenths per cent.) is passed, when, owing probably to the endothermic formation of non-crystalline cementite, the heat of solution increases again, but never reaches that of pure iron. The presence of manganese, when combined with carbon in annealed metal, diminishes very markedly the heat of solution, owing to the greater stability of the compounds of manganese and carbon compared with that of the corresponding compounds of iron. If there is not sufficient carbon to combine with the manganese, or if the carbon is above the saturation point, the substitution of manganese for iron seems to increase the heat of solution slightly, owing to the higher heat of formation of manganous chloride compared with that of ferrous chloride. In the quenched metal, manganese seems to behave exactly the reverse of that in the annealed steel, the effect being to very notably increase the heat of solution, the increase being more marked the higher the temperature from which the steel is quenched. Phosphorus plays a considerable part in determining the heat of solution.

Some results obtained with copper confirm those of Osmond, that heat treatment has but slight influence on the heat of solution.

The influence of reheating, or tempering, hardened steel on its heat of solution was also investigated. The reheating was carried out either in a hydrogen or nitrogen atmosphere. The heat of solution decreases, and the apparent percentage of carbon, as indicated by the colour test, increases with the temperature to which the metal is reheated, until the critical point *Ac* is passed. The hydrogen then seems to combine with the carbon, and the heat of solution rises very markedly. When the gas used is nitrogen, the temperature being over 1000°, the nitrogen removes the carbon, part at least forming cyanogen, and the heat of solution of the metal is very much lowered. The diminution in tensile strength is almost exactly proportional to the diminution in the heat of solution.

H. C.

Determinations of the Density of Small Volumes of Gases. By TH. SCHLÖSING, junr. (*Compt. rend.*, 1898, 126, 220—223).—The author has devised an apparatus for the determination of the density of gases that are only available in small quantity. It is an adaptation of the vertical tube apparatus frequently used in the case of liquids, and consists of two tubes 1.1 to 1.6 metres long, and 2.0 to 2.5 mm. in diameter, these dimensions being selected with a view to minimise diffusion. At the bottom, the tubes are connected, by means of a three-way stopcock, with one another and with a reservoir containing mercury. At the top, each tube is bent at a right angle, and can be connected either with a U-shaped absorption bulb or with a horizontal tube, the function of which is to prevent the entrance of air into the vertical tubes. For the greater part of their length, the vertical tubes are enclosed in a wide tube, through which a current of water is passed.

Suppose the gas, G , whose density is to be determined, is lighter than carbonic anhydride, has no action on it, and is not absorbed by potassium hydroxide solution. One vertical tube, A , is completely filled with carbonic anhydride, and the other B , with the gas under examination, and communication is established between the two tubes, their upper ends being open to the air. Some of the carbonic anhydride passes into the lower part of the tube B , and drives out some of the gas G , whilst air is drawn into the upper part of A . After waiting about 10 minutes, to allow equilibrium to be established, without giving time for the gases to mix by diffusion, communication between the two tubes is cut off.

Let α and β be the surfaces at which respectively air and carbonic anhydride, and the gas G and carbonic anhydride would be in contact if they did not mix at all, h and h' the vertical distances of α and β from the centre of the open ends of the tubes, and d , d' , and δ the respective densities of air, the gas G , and carbonic anhydride, in the dry state and at the particular temperature and pressure. The weights of the gas in the tubes A and B between β and the centre line of the upper apertures are the same, and $h'd' = hd + (h' - h)\delta$, for if the insides of the tubes were moistened all the gases are saturated with water vapour. Moreover, the densities of all the gases, under the conditions of the experiment, differ from their densities under standard conditions by the same factor. Hence $h'd'_0 = hd_0 + (h' - h)\delta_0$. In the case under consideration, $d = 1$ and $\delta = 1.529$. To determine h and h' , each tube is connected with an absorption bulb containing potassium hydroxide solution, and the whole of the gas from each tube is passed into the potassium hydroxide solution until the whole of the carbonic anhydride has been absorbed. The residual gases are then brought back into their respective tubes, and adjusted to atmospheric pressure. The points at which the mercury stands are α and β , and these determine h and h' . The results obtainable in this way will be discussed in a later paper.

C. H. B.

Densities of Small Quantities of Gases. By TH. SCHLÆSING, junr. (*Compt. rend.*, 1898, 126, 476—479).—The author has determined the densities, with reference to air, of several gases, by means of the apparatus previously described (preceding abstract), working with 5 to 7 c.c. of gas and using carbonic anhydride as the third gas.

	Air.	Nitrogen.	Oxygen.	Argon.	Methane.
Density found ...	1	0.967	1.105	1.376	0.559
Real density	1.000	0.967	1.105	1.376	0.558

It was found that equilibrium was attained in from 4 to 6 minutes, and with a longer time the influence of diffusion began to be recognisable. When the density is taken with successive fresh quantities of gas, allowing 2, 4, 6, 8 minutes for the establishment of equilibrium, the density obtained at first decreases with the time allowed, remains constant with periods of 4 to 6, or sometimes 8, minutes, and then again diminishes.

With hydrogen, diffusion is so rapid that good results cannot be obtained. The tubes used varied from 1.15 m. to 1.65 m. in height and from 1.6 mm. to 2.7 mm. in diameter.

C. H. B.

Mixtures of Gases. By ANATOLE LEDUC (*Compt. rend.*, 1898, 126, 218—220).—The author proposes to substitute for the well-known law of partial pressures, which is not in absolute agreement with the facts, the statement that *the volume occupied by a mixture of gases is equal to the sum of the volumes occupied by its constituents under the particular temperature and pressure.* In a mixture of gases, each constituent should be regarded as subject to the total pressure, and not simply to the pressure, it would itself exert if it were alone in the vessel. The volumetric composition of air calculated from the densities of oxygen and atmospheric nitrogen agrees with the actual determinations, but the composition calculated from the law of partial pressures is distinctly inaccurate. Direct experiments show that when carbonic anhydride (2 vols.) and nitrous oxide (1 vol.) are mixed there is no change in volume or pressure, whilst the old law would require an increase in pressure of 2.3 mm. On the other hand, with carbonic anhydride and sulphurous anhydride, under similar conditions, there is an increase in pressure of 1.25 mm., but this is only about one-quarter of the increase regarded by the old law. The difference between the density of argon as calculated by the author on the basis of his law of volumes, 19.80, and that determined by Rayleigh and Ramsay, 19.94, is probably due to the fact that, when nitrogen and argon are mixed, there is an increase in pressure (or volume). C. H. B.

Geissler's Densimeter. By M. LEFEBVRE (*Chem. Centr.*, 1897, ii, 402—403).—The apparatus consists of two U-tubes whose shorter, graduated limbs are joined at the top; a stop-cock inserted at the junction communicates with the air, and the bottom of each U-tube is provided with a tap. To determine the specific gravity of a liquid, the middle cock is opened, water is run into the one tube (whose graduations read from below upwards) and the given liquid into the other (graduated from above downwards) until the liquid surface in each tube stands at zero. The middle cock is then closed and water added to the tube which contains water until the surface in the longer tube reaches a certain height. From the difference of the levels of the liquids in the tubes, the specific gravity of the given liquid is easily calculated. E. W. W.

Determination of Dissociation Constants by the Increase of Solubility. By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1898, 25, 385—418).—The solubility of an acid in water is increased by the addition of small quantities of a base, and this increase being dependent on the dissociation of both base and acid, may serve as a means of determining the dissociation of the acid if that of the base is known, and *vice versa*; the necessary equation is deduced in the paper. The availability of the method was first proved by the determination of the dissociation of aniline and paratoluidine by their addition to solutions of cinnamic and paranitrobenzoic acids. The value obtained by means of these two acids agreed satisfactorily with one another and with those of Bredig (*Abstr.*, 1894, ii, 229), whilst the close agreement of the values obtained by the use of various concentrations indicated the possible accuracy of the method. It is available for bases of very varying degrees of dissociation, but the details of the experimental

method differ according to the solubility of the compounds. The dissociation-degrees of the nitranilines were determined with the aid of paranitrobenzoic and parabromobenzoic acids; the values 4.2×10^{-12} and 5.3×10^{-2} were obtained for metanitriline, and 1.1×10^{-12} and 1.3×10^{-12} for paranitriline. In the case of the ortho-base, the increase of solubility of the acids employed was too small, and hydrochloric acid was therefore used, when the value 0.015×10^{-12} was obtained. The influence of the nitro-group in weakening the basic character of aniline is hence weakest in the meta-position, a result in accord with its influence on the acidity of benzoic acid. The dissociation of ψ -cumidine was also determined by means of parabromobenzoic acid, and the value 1.7×10^{-9} was obtained; the constant for paratoluidine is 2.05×10^{-10} so that the further entrance of methyl groups has but little effect on the basicity. L. M. J.

Apparatus for Determining the Solubility of Substances in Boiling Liquids. By HEINRICH GÖCKEL (*Chem. Centr.*, 1897, ii, 401—402; from *Forsch.-Ber. Lebensm.*, 4, 173—177).—The solvent is boiled with the substance to be dissolved in a flask which is fitted with a reflux condenser and contains a small filter-tube in which cotton-wool is placed; during the boiling, this tube serves to conduct a current of air whereby the liquid is stirred and also prevented from entering the filter. A portion of the saturated solution may be withdrawn from the flask for examination, by forcing the liquid through the filter into a second flask also fitted with a condenser, deposition of the substance in transit being prevented by surrounding the connecting tube with liquid maintained at a temperature 1° or 2° higher than the boiling point of the solvent.

By means of this apparatus, the author has obtained the following data for the solubility of caffeine in various liquids in each case at 18° and at the boiling point respectively. One part of caffeine dissolves in 839 and 339 parts of ether; in 109.8 and 18.9 of benzene; in 8.5 and 6.4 of chloroform; in 1123 and 142.4 of carbon tetrachloride. Theobromine is quite insoluble in carbon tetrachloride or anhydrous ether at 18° , but at the boiling point 1 part is dissolved in 4703 and 3125 parts of these liquids respectively. E. W. W.

Combination and Substitution. By F. WALD (*Zeit. physikal. Chem.*, 1898, 25, 525—535).—A continuation of the author's previous theoretical papers on the application of Gibbs' phase law to chemical processes (this vol., ii, 159.)

Mass Action and the Phase Law. Function of the Solvent in Chemical Reactions. By BASIL B. KURILOFF (*Zeit. physikal. Chem.*, 1898, 25, 419—440).—The partition ratio of acetic acid dissolved in water and benzene is apparently not constant, being a function of the concentration, but if the dissociation is allowed for and the partition ratio calculated for the undissociated molecules only, a constant value is obtained. Hence, if a system AB , dissociable into A and B be dissolved in liquid (1) and c_1, c_2, c_3 , be the concentrations of the complex and component groups, $K_1 c_1 = c_2 c_3$ where K_1 is the velocity constant of the reaction; similarly, in a second solvent, (2)

the equation $K'_1 c'_1 = c'_2 c'_3$ obtains. If k_1, k_2, k_3 be the partition ratios for the three molecular groups, it follows that $k_1 = k_2 k_3 K'_1 / K_1$, and as the partition ratio is equal to the ratio of the solubilities in the two solvents, the solubility in one may be calculated if the remaining constants are known. The author has tested this deduction experimentally in the case of solutions of β -naphthol picrate in benzene and in water. The reaction constant for the equation β -naphthol picrate $\rightleftharpoons \beta$ -naphthol + picric acid was found to be 4466 in aqueous solution at 29.5° and 3607 at 12.5° ; in benzene solution, the constant is 18220 and the solubility was found to be 0.0308 gram-molecules per litre. In determining the partition ratio of the picric acid, the dissociation in water was allowed for and the value 39 obtained, whilst for β -naphthol the ratio was about 67, all constants being found for 29° . It hence follows that the solubility of the β -naphthol picrate in water is given by the expression $18220 \times 0.0308 / 4466 \times 39 \times 67$, that is, 0.000047 mol. per litre. The experimental determination of the solubility of the undissociated picrate is difficult, and the author attempted to obtain it from (1) the changes in the composition of the solution in equilibrium with β -naphthol picrate by the addition of β -naphthol or picric acid, (2) the difference in the solubility of β -naphthol by the addition of the picrate. The results are, however, not entirely free from doubt, and indicated a solubility of the undissociated compound varying from 0.00007 to 0.00008. The 29° isotherms for the aqueous and benzene solutions are given, and it is seen that if these be taken for undissociated molecules only, the curves for the two solutions become very similar and almost identical in form.

L. M. J.

Influence of the Medium on the Velocity of Reaction in Gaseous Systems. By ERNST COHEN (*Zeit. physikal. Chem.*, 1898, 25, 483—496).—It has been shown by Menschutkin and by Carrara that the velocity of reaction in liquid systems is profoundly modified by the use of different solvents (Abstr., 1894, ii, 310), and the effect varies with different reactions, the velocity of reaction of triethylamine and ethylic iodide being greater in acetone than in ethylic or methylic alcohol, whilst that of diethylic sulphide and ethylic iodide is far greater in the alcoholic than in the acetone solution. The author, therefore, investigated the effect of indifferent gases on a gaseous reaction velocity, and the decomposition of arsenic trihydride was chosen for the purpose, the author having previously shown that the velocity of reaction becomes constant in this case as soon as the walls of the containing vessel are completely coated with arsenic (Abstr., 1896, ii, 593). The apparatus employed was essentially identical with that employed originally by van't Hoff and Kooy, and the velocity was determined for arsenic trihydride alone, and for mixtures of this gas with hydrogen and with nitrogen, but neither gas had any effect on the velocity of reaction, a result predicted by Nernst (*Theor. Chem.*). It was also shown that the velocity of the reaction is very greatly reduced if the walls of the vessel are thoroughly cleaned by 'aqua regia,' being reduced to about one-tenth of the original value.

L. M. J.

NOTE.—It may be noted that the influence of an admixed gas is not at all comparable with that of a solvent in liquid systems, as in Menshutkin's and Carrara's experiment, since the solvents have varying dissolving and ionising effects on the various reacting compounds, and are hence not indifferent substances.

L. M. J.

Speed of Reduction of Ferric Alum by Sugar. By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1897, 19, 683—698).—In a mixture of ferric alum and sugar, inversion of the sugar and reduction of the iron salt take place rapidly on warming, or even on standing in bright sunlight through several warm days. The speed of the reduction was measured by the determination of resistances from time to time, the results being compared with the resistances found from known mixtures of acid, ferric and ferrous salts, and ammonium sulphate. The speed is found to be an accelerated one, the cause of the acceleration being the sulphuric acid liberated as the reduction advances. If A represents the ferric salt present at the beginning of the experiment, and x that reduced at the time t , and B is the amount of sugar, the speed is given by the equation $dx/dt = K(B+x)(A-x)$.

H. C.

Equilibrium in the System, Water, Ether, and Ethylenic Cyanide. By FRANS A. H. SCHREINEMAKERS. (*Zeit. physikal. Chem.*, 1898, 25, 543—567).—The equilibrium between water and the other components had been previously determined (*Abstr.*, 1897, ii, 483; this vol., ii, 156) and a few points on the equilibrium curve of the cyanide and ether were first obtained. In the case of the system with the three components, a quintuple point exists at 4.5° , where ice, solid ethylenic cyanide, and two liquid phases co-exist, or, representing liquids in which water, ether, and the cyanide respectively predominate, by L_w , L_e , and L_c , the equilibrium at this quintuple point is that of ice + cyanide + L_e + L_w . With rise of temperature, the change, ice + cyanide + $L_e \rightarrow L_w$ occurs, and at the point four, equilibrium fields meet, namely, those of ice + cyanide + L_e ; ice + cyanide + L_w ; ice + L_e + L_w and cyanide + L_e + L_w , the latter existing at temperatures above -4.5° , the first at temperatures below -4.5° . The further changes of these equilibrium systems were investigated, and it was found that, in the case of the field, cyanide + L_e + L_w , a new quintuple point occurs at the temperature $1-2^\circ$, where, owing to the liquefaction of the solid cyanide, the equilibrium is that of the system, solid cyanide + L_e + L_w + L_c . The composition of each of the three liquid phases was determined; $L_e = 7.5$ mols. water + 87.5 mols. ether + 4.8 mols. ethylenic cyanide; $L_w = 95.1$ mols. water + 3.1 mols. ether + 1.6 mols. ethylenic cyanide; $L_c = 27.9$ mols. water + 16.4 mols. ether + 55.6 mols. ethylenic cyanide. On heating, the change $N + L_e + L_w \rightarrow L_c$ occurs; four equilibrium fields occur, and these were further investigated. To trace the further equilibrium of the three liquid phases, various mixtures were prepared and heated, and it was found that at 56.5° the phases L_w and L_c become identical, and two liquid phases hence result. A number of diagrams of the isothermals at various temperatures are given, and are necessary for the discussion of the experimental results.

L. M. J.

Decomposition of Triglycerides with Dilute Acids. By ADOLF C. GEITEL (*J. pr. Chem.*, 1898, **57**, 113—131. Compare Abstr., 1897, i, 546).—The velocities of hydrolysis of mono-, di-, and tri-acetin with dilute hydrochloric acid have been determined, and are found to be in the proportions 1:2:3. Mathematical equations are given which hold good, not only for the decomposition of the triglycerides, but also in general for all bimolecular reactions, with measurable velocity, leading to the formation or decomposition of tri-derivatives.

The paper is principally a theoretical one of a physico-chemical nature.

A. W. C.

Dependence on Temperature of the Number of Crystallisation Nuclei which form in Supercooled Liquids. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1898, **25**, 441—479).—If a melted solid is strongly supercooled, and then kept at a higher temperature below its melting point, crystallisation proceeds from a number of nuclei, and the author endeavoured to determine the effect of the supercooling and the time of exposure on the number of nuclei. For the quantitative experiments, betol and piperine were chiefly employed, but experiments were also performed with allylthiocarbamide, chloralurethane, cinchonidine, dulcitol, mannitol, narcotine, *d*-camphoric acid, resorcinol, santonin, and vanillin. The number of crystallisation points is very small in proportion to the number of molecules present, not exceeding 1000 per minute per cubic mm., and increases with increased supercooling until it attains a maximum, then decreases. The temperature of this maximum always occurs in the temperature interval in which the velocity of crystallisation decreases with fall of temperature, and is only very slightly altered by the presence of foreign substances, although the actual number of the points of crystallisation may be greatly changed, in either direction, by the presence of small quantities of either soluble or insoluble compounds. Various modifications of crystalline aggregates may occur, each having its own maximum, that of the more stable modification being usually lower than that of the less stable form, and the addition of a foreign substance frequently causes the disappearance of one form and increase of the other. About 150 compounds were also qualitatively examined, and it was found that about one-third of these could by very speedy supercooling be obtained as glassy masses, and the author considers it probable that all compounds could be so obtained by sufficiently rapid cooling.

L. M. J.

Velocity of Crystallisation. By FRIEDRICH W. KÜSTER (*Zeit. physikal. Chem.*, 1898, **25**, 480—482).—The explanation of the crystallisation of overcooled liquids offered by Tammann (Abstr., 1897, ii, 444) indicates constancy of the velocity of solidification, and although this obtains if the overcooling is sufficiently great, yet it is at first approximately proportional to the overcooling, and the author therefore offers an explanation more in accord with experimental facts.

L. M. J.

Convenient Gas Generator. By THEODORE W. RICHARDS (*Amer. Chem. J.*, 1898, **20**, 189—195).—The principle adopted by the author is to remove the exhausted solution from the lower part of the gene-

rator by taking advantage of its increased density, and to supply fresh liquid by means of a tube or perforations situated in the upper part of the generator. Several modifications of the apparatus are described, the advantages claimed being that the fresh material is kept uncontaminated with that which has been exhausted, and that variations of pressure are minimised. A similar device is made use of for rapidly dissolving crystals; the "dissolver" in which the crystals are placed consists of a cylindrical funnel, the sides of which are perforated at the top; it is completely immersed in the solvent, contained in a deep, narrow cylinder, and in the bottom of the latter the heavy liquid formed by the dissolved salt collects.

W. A. D.

Inorganic Chemistry.

Composition of Air in Various Places: Densities of Gases.
By ANATOLE LEDUC (*Compt. rend.*, 1898, 126, 413—416).—The author has determined the composition of air from various localities by his method of weighing the air and calculating the proportions of oxygen and nitrogen from their densities. The percentage of oxygen by weight was as follows:—Paris 23·20; Nice, Nîmes, Algiers, in summer, 23·23; near Dieppe, July, 23·16, April, 23·07; Belgian frontier, summer, 23·17, winter, 23·09; Alps (2060 metres), violent descending wind in October, 23·05, ascending breeze on following day, 23·23; Puy de Dôme, November, calm, 23·17, November, with strong south-west wind, 23·23.

The author considers that the air of London is somewhat less rich in oxygen than the air of Paris, and that this explains the fact that Lord Rayleigh's densities of gases as compared with air are always somewhat higher than his, whereas when oxygen is taken as the unit both sets of results agree. On this assumption, London air contains 23·1 per cent. by weight of oxygen.

	Density, air = 1.		Density, oxygen = 1.	
	Rayleigh.	Leduc.	Rayleigh.	Leduc.
Oxygen.....	1·10535	1·10523	1	1
Atmospheric nitrogen.....	0·97209	0·97203	0·87944	0·87948
Chemical nitrogen	0·96737	0·96717	0·87507	0·87508
Carbonic oxide	0·96716	0·96702	0·87498	0·87495
Carbonic anhydride	1·52909	1·52874	1·3833	1·3832

Lord Rayleigh's number for carbonic anhydride was corrected for compressibility, the determinations having been made at a pressure above normal, and his value for chemical nitrogen was recalculated, leaving out the results obtained with nitrogen prepared by decomposing nitrogen peroxide.

C. H. B.

Hypertitanates and Hyperborates. By PETR G. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 1898, 31, 678—680).—Sodium hyperborate, $\text{NaBO}_3 + 4\text{H}_2\text{O}$, is readily obtained when a saturated solution of borax containing an equivalent quantity of sodium hydroxide is treated with an excess of hydrogen peroxide (double the amount calculated for NaBO_3); after some time, large, transparent crystals of the salt separate. It is stable at the ordinary temperature, and dissolves in water without undergoing decomposition, but its aqueous solution, on warming, evolves oxygen. 100 grams of water dissolve 1.17 grams of the salt.

When a solution of borax and alkali is treated with half the amount of hydrogen peroxide mentioned above, kept at 40° , then cooled and treated with alcohol previously cooled to -10° , a white, crystalline, unstable compound is obtained; it is readily soluble in water, but undergoes decomposition evolving oxygen and yielding crystals of the hyperborate, $\text{NaBO}_3 + 4\text{H}_2\text{O}$.

Potassium peroxide hypertitanate, $\text{K}_2\text{O}_2 \cdot \text{TiO}_3 \cdot \text{K}_2\text{O}_4 + 10\text{H}_2\text{O}$, is obtained when well-cooled hydrogen peroxide and the requisite quantity of potassium hydroxide are added to pertitanic anhydride. On the addition of well-cooled alcohol, minute crystals are obtained, which may be washed with cooled alcohol and ether, and pressed on a cold porous plate. They are stable at 0° , but deliquesce at ordinary temperatures and give up oxygen.

Sodium peroxide hypertitanate, $(\text{Na}_2\text{O}_2)_4 \cdot \text{Ti}_2\text{O}_7 + 10\text{H}_2\text{O}$, crystallises in small, colourless prisms; it does not liberate iodine from potassium iodide. When dissolved in water, it evolves oxygen, and when placed over sulphuric acid it loses both water and oxygen. J. J. S.

Reduction, Electrolysis, and Photolysis of Carbonic Anhydride. By A. BACH (*Compt. rend.*, 1898, 126, 479—481).—Lieben has shown that when carbonic anhydride is reduced by sodium amalgam in an alkaline solution, formic acid is the sole product. The author finds that when carbonic anhydride in aqueous solution is reduced by means of hydrogen occluded in palladium, some formaldehyde is also produced. In the electrolysis of carbonic acid, the chemical changes are represented by the equation $3\text{H}_2\text{CO}_3 = 2\text{CO}_3 + 2\text{H}_2\text{O} + \text{CH}_2\text{O} = 2\text{H}_2\text{CO}_3 + \text{O}_2 + \text{CH}_2\text{O}$, and the author has shown (*Abstr.*, 1893, 483) that, under the influence of sunlight, the acid decomposes thus, $3\text{H}_2\text{CO}_3 = 2\text{H}_2\text{CO}_4 + \text{CH}_2\text{O} = 2\text{H}_2\text{CO}_3 + \text{O}_2 + \text{CH}_2\text{O}$. Assuming that in the electrolysis the acid is reduced by the liberated hydrogen, the decompositions by electrolysis and photolysis are identical, for it is obvious that the group $\text{CO}_3 + \text{H}_2\text{O}$ is equivalent to the percarbonic acid H_2CO_4 , but it remains uncertain whether the solar radiations merely act in the same way as electricity or are transformed into electricity. C. H. B.

Conditions of Formation of Carbides of the Alkali and Alkaline-Earth Metals and of Magnesium. By HENRI MOISSAN (*Compt. rend.*, 1898, 126, 302—308).—Potassium and sodium carbides are obtained in very small quantities only by the action of the electric arc on mixtures of the respective metals and

their carbonates, even when the intensity of the arc is low. Both carbides are, in fact, dissociated at a temperature considerably lower than that of the arc. Lithium carbide is more stable, but yet is decomposed somewhat readily; calcium carbide can be completely decomposed, even in presence of excess of carbon, by an arc from a current of 1200 ampères and 60 volts without volatilising the carbon; magnesium carbide is decomposed by the arc from a current of 600 ampères and 60 volts, and, like the carbides of sodium and potassium, cannot be prepared in the electric furnace.

Potassium is slowly attacked by acetylene at the ordinary temperature and pressure, the action in time being complete; hydrogen is liberated, and the compound C_2HK is formed. Sodium behaves similarly, but the action of acetylene gas at the ordinary temperature and pressure is extremely slow. With liquid acetylene at the ordinary temperature, the action is much more rapid, and, after many days, is complete. The compressed gas behaves similarly, and the rate of action seems to be a function of the pressure. Under ordinary pressure, the action of the gas on the metal is very distinct at 50° , and at 70° small fragments of sodium are completely converted into the compound C_2HNa after about 15 days.

The compounds C_2HK and C_2HNa are white solids, which are readily decomposed by water, with liberation of acetylene. When heated, they give off acetylene, and are converted into the carbides, C_2K_2 and C_2Na_2 , which decompose into carbon and hydrogen if heated to redness in a vacuum.

C. H. B.

Decomposition of Strontium Thiosulphate and Sulphite by Heat, and Production of Phosphorescent Strontium Sulphide. By JOSÉ R. MOURELO (*Compt. rend.*, 1898, 126, 420—423).—Strontium thiosulphate begins to decompose at a red heat, and if kept at bright redness for 3 hours it is completely converted into sulphate, which is very slightly phosphorescent. At a somewhat lower temperature, decomposition takes place in accordance with the equation $4SrS_2O_3 = SrS + S_4 + 3SrSO_4$, and the product contains strontium sulphide, 15.02; sulphur, 16.12; strontium sulphate, 68.45 per cent. It shows a yellowish-green phosphorescence which has its maximum intensity when the product has the composition indicated. Strontium sulphite behaves similarly, and yields a mixture of sulphide and sulphate, which shows a maximum intensity of phosphorescence when it has the composition, sulphide 14.05, sulphate 85.94 per cent.

In these cases, the phosphorescent material is mixed with a large proportion of a non-phosphorescent compound, and possibly the latter has the same function as the inert substances in the cases investigated by Lecoq de Boisbaudran (*Abstr.*, 1890, 435). The intensity of the phosphorescence of the strontium sulphide mixtures is not materially affected by the addition of a considerable proportion of sodium chloride.

The products from both the sulphite and the thiosulphate alter somewhat rapidly when exposed to air owing to the oxidation of the finely divided strontium sulphide.

C. H. B.

Atomic Weight of Zinc. By HARMON N. MORSE and H. B. ARBUCKLE (*Amer. Chem. J.*, 1898, 20, 195—202).—In view of the observation of Richards and Rogers (*Abstr.*, 1894, ii, 45), that zinc oxide prepared by igniting the nitrate always retains nitrogen and oxygen, even when strongly heated, the authors have repeated the experiments of Morse and Burton (*Abstr.*, 1888, 1247) on the atomic weight of zinc, taking into account the weight of both oxygen and nitrogen which remains occluded. This was estimated by measuring the gas evolved on dissolving the zinc oxide formed in each experiment in dilute sulphuric acid from which all gases had been removed by exposure for several days in a vacuum. The oxygen was determined by explosion with hydrogen; the gas remaining was found to contain free nitrogen only.

None of the nitrogen appears to be retained by the zinc oxide as nitride, and the occlusion of gases appears to be solely due to physical causes; the authors cannot confirm the statement of Richards and Rogers, that, on heating, the imprisoned oxygen escapes more readily than the nitrogen.

The average of eight experiments, ranging from 65.437 to 65.489 gives 65.457 as the corrected value for the atomic weight of zinc, that of oxygen being taken as 16.

W. A. D.

Colour of Amorphous Mercurous Iodide. By MAURICE FRANCOIS (*J. Pharm.*, 1897, [vi], 6, 529—533).—Mercurous iodide quite free from mercuric iodide and also from metallic mercury may readily be obtained by the following method:—125 grams of mercurous nitrate is dissolved in 2 litres of water to which 20 c.c. of nitric acid has been added. A solution of 50 grams of potassium iodide in 100 c.c. of distilled water is run in drop by drop with constant stirring; the mixture is then shaken for some 15 minutes, and the precipitate, which at first has a greenish-yellow appearance, changes to clear yellow. The precipitate is left in contact with the mother liquor for 24 hours in the dark, is then washed some 12 times by decantation in the dark, 2 litres of water being used for each washing, and is finally transferred to a filter paper and dried at 50°. As thus obtained, mercurous iodide is of a pure yellow colour with no shade of green. The ordinary green iodide consists of a mixture of mercurous iodide with metallic mercury.

J. J. S.

Action of Hydrogen Arsenide on Mercuric Chloride. By ALFRED PARTHEIL and E. AMORT (*Ber.*, 1898, 31, 594—595).—This reaction, in aqueous or alcoholic solution, is known to give rise to the formation of the yellow compound $\text{AsH}(\text{HgCl})_2$ and the brown $\text{As}(\text{HgCl})_3$ in succession; attempts to prepare the compound $\text{AsH}_2 \cdot \text{HgCl}$ have been unsuccessful, but by continuing to pass hydrogen arsenide into the alcoholic solution, a black precipitate of the composition As_2Hg_3 was obtained.

C. F. B.

Constitution of Inorganic Compounds. XII. Anhydro-oxycobaltamine and Oxycobaltamine Salts. By ALFRED WERNER and ALB. MYLIUS (*Zeit. anorg. Chem.*, 1898, 16, 245—267).—*Anhydrooxycobaltamine salts.*—The nitrate, $\text{Co}_2\text{O}_2(\text{NH}_3)_{10}(\text{NO}_3)_5$, is

obtained as follows:—50 grams of cobalt carbonate, dissolved in the necessary quantity of dilute nitric acid, is mixed with 200 grams of ammonium nitrate, and filtered, mixed with 600 c.c. of ammonia (20 per cent.) and treated with a current of air for 36 to 48 hours until the solution no longer smells strongly of ammonia. The black solution, which contains crystals of Frémy's oxycobaltammine nitrate, is evaporated to a magma in a current of air, mixed with nitric acid, and the salt separated by filtration, and washed with cold dilute nitric acid until the filtrate is colourless. The anhydroxycobaltammine nitrate is completely insoluble in dilute nitric acid, whereas it is quickly decomposed by pure water. It crystallises from hot dilute nitric acid (20 c.c. acid to 1000 c.c. water) in black, lustrous needles. The *chloride*, with H_2O , obtained by triturating the nitrate two or three times with cold concentrated hydrochloric acid, crystallises from hot dilute hydrochloric acid in long, green needles.

Anhydroxycobaltammine nitrate, when treated with ammonia, yields a brownish-red solution, from which hexamminecobalt nitrate separates on cooling; the filtrate, when treated in the cold with concentrated hydrochloric acid, at first yields a brownish-red precipitate of chloropentamminecobalt chloride, and the filtrate from this, after about 3 hours, deposits a small quantity of a black, insoluble chloride which has not been further examined.

Anhydroxycobaltammine nitrate, when triturated with a cold solution of potassium cyanide, yields a *cyanide* of the composition $\text{Co}_2\text{N}_{10}\text{C}_6\text{H}_{21}\text{O}_9$, with evolution of ammonia and hydrogen cyanide. This cyanide is easily soluble in excess of potassium cyanide, and cannot be isolated from such a solution; it is necessary, therefore, to take care that only just sufficient potassium cyanide is used in preparing it. The product is cautiously washed with water, very dilute sulphuric acid, and ammonia until the filtrate is colourless, then dissolved in a concentrated solution of potassium thiocyanate, and precipitated with absolute alcohol. It is a cherry-red powder, and when warmed with silver nitrate solution, yields hexamminecobalt nitrate and cobalt silver cyanide.

When anhydroxycobaltammine nitrate is dissolved in an excess of sulphurous acid, a red solution is obtained, and this, when evaporated in a vacuum, yields red crystals of aquopentamminecobalt nitrate. If heated with concentrated hydrochloric acid, 48 per cent. of the anhydroxycobaltammine nitrate is converted into chloropentamminecobalt chloride and 52 per cent. into cobalt sulphate (after treating the filtrate from the chloride with sulphuric acid). When heated with nitric acid, aquopentamminecobalt nitrate is obtained.

Oxycobaltammine Salts.—When oxycobaltammine nitrate is dissolved in an excess of sulphurous acid, a red solution is obtained, which, if heated with concentrated hydrochloric acid, yields only a small quantity of chloropentamminecobalt chloride, about 5 per cent. of the nitrate being converted into this compound. The filtrate from the chloropentamminecobalt chloride, after evaporation and treatment with sulphuric acid, yields cobalt sulphate corresponding with about 93 per cent. of the oxycobaltammine nitrate. This reaction with sulphurous acid, therefore, provides an easy means of distinction between anhydroxycobaltammine salts and oxycobaltammine salts.

The author was unable to obtain roseocobaltpentammine chloride, as described by Vortmann, by heating oxycobaltammine nitrate at 110° . Oxycobaltammine nitrate is prepared as follows. Cobalt nitrate (200 grams) is dissolved in water (250 grams), the boiling solution poured into ammonia (850 grams, sp. gr. = 0.927), and the mixture heated for about 5 minutes; when cold, the mixture is filtered and treated with a slow current of air as long as a thick, crystalline precipitate is formed. The crystals of the oxycobaltammine nitrate are collected, washed with concentrated ammonia and alcohol, and dried by pressing between filter paper. After heating at 110° until the weight is constant, the product is treated with a small quantity of water, and the brown filtrate mixed with concentrated hydrochloric acid; after a time, a brown precipitate is obtained, consisting of a mixture of melanocobalt chloride, hexamminecobalt chloride, and aquopentamminecobalt chloride. The melanocobalt chloride, which is formed in small quantities only, remains undissolved when the mixture is treated with water. The solution containing the other two salts is boiled with hydrochloric acid, when the chloropentammine chloride is precipitated from the hot solution, and the hexammine chloride separates on cooling. This operation must be repeated several times in order to effect a complete separation. When the brown aqueous solution obtained from the product from the oxycobaltammine nitrate, after heating at 110° , is treated with nitric instead of with hydrochloric acid, hexamminecobalt nitrate is obtained, and on adding hydrochloric acid to the filtrate from this salt, chloropentamminecobalt chloride is precipitated. E. C. R.

Sodium Sulphochromite [Thiochromite]. By R. SCHNEIDER (*J. pr. chem.*, 1898, 57, 208).—The author (this vol., ii, 229) omitted to mention Gröger's prior preparation of sodium thiochromite (*Wien. Acad.*, 1881, 83, 749); the salt, however, was described in the red, amorphous condition, and not in the crystalline form.

A. W. C.

Atomic Weight of Tungsten. By WILLETT L. HARDIN (*J. Amer. Chem. Soc.*, 1897, 19, 657—676).—The author discusses the results obtained by others for the atomic weight of tungsten, and emphasises their lack of concordance; it is pointed out that even amongst the results obtained by the same experimenter serious deviations exist. The method usually adopted has been to reduce the trioxide to the metal, and subsequently to reoxidise this by ignition; the author now describes over 60 determinations by the same method. The tungsten trioxide employed was prepared by strongly igniting ammonium tungstate obtained from wolframite from Zinnwald, Bohemia, which had been carefully purified and freed from molybdenum; the reduction was effected at a very high temperature by means of purified hydrogen. The maximum deviation of the first four results by reduction in a hard glass tube was 0.35, whilst the mean value of the atomic weight was 184.10 ($0 = 16$); in a porcelain tube the maximum difference was 0.28, and the atomic weight 183.84 . On reoxidising, much higher results were obtained; the mean of six results gave 184.77 for the atomic weight, with a deviation of 0.85. The oxide obtained in these experi-

ments was then reduced, a maximum deviation of 1.03 being found in eight experiments, which gave a mean of 184.40 for the atomic weight; on reoxidation, a variation of 0.64 was found in three experiments.

In the later experiments, the hydrogen used in the reduction was carefully freed from air, and the metal allowed to cool in a vacuum; a variation of 0.7 was, however, found in seven results, which gave a mean value of 184.01 for the atomic weight; and the values obtained by weighing the water formed in the reduction were equally discordant. Eight reductions of the trioxide obtained from New Zealand scheelite gave a mean of 183.74, with a maximum deviation of 0.20; on oxidation, the results varied by 0.45, and gave a mean of 183.94. Material obtained from Connecticut wolframite gave means of 183.64 and 184.18 in three experiments by reduction and oxidation respectively; that obtained from Colorado hübnerite and Bohemian scheelite gave as the mean of two experiments with each, by reduction and oxidation, 183.92, 183.99, 183.76, and 184.12.

From the author's investigations it appears that tungsten attacks the vessels, either porcelain or platinum, in which the determinations are made, that tungsten trioxide is either slightly volatile or is mechanically carried off by the hydrogen during reduction; and that it contains appreciable quantities of nitrogen and, probably, hydrogen. Hence, taking into account also the varying nature of his results, the author concludes that the method employed must be considered unsatisfactory.

W. A. D.

The Salts of Pertungstic Acid and Permolybdic Acid. By PETR G. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 1898, 31, 632—636).—The salts described were obtained by adding cooled hydrogen peroxide and aqueous soda or potash to a cooled solution of a pertungstate or permolybdate, precipitating with alcohol at -12° , and drying the resulting salt in the air. When sodium pertungstate (1 mol.) is treated with soda (3 mols.) and excess of hydrogen peroxide, a yellow salt is obtained of the composition $\text{Na}_2\text{O}_2 \cdot \text{WO}_4 \cdot \text{H}_2\text{O}_2 + (\text{Na}_2\text{O}_2)_2 \cdot \text{WO}_4 + 7\text{H}_2\text{O}$. On prolonged exposure to the air, it loses oxygen and water, and at the same time becomes white. Water produces a vigorous evolution of oxygen, and the solution formed contains hydrogen peroxide. When only half the amount of soda is taken and a large excess of hydrogen peroxide employed, an unstable salt, $\text{Na}_2\text{O}_2 \cdot \text{WO}_4 \cdot \text{H}_2\text{O}_2$, is obtained, which explodes feebly when heated. The salt produced by the action of potash and hydrogen peroxide on potassium pertungstate has the formula $\text{K}_2\text{O}_4 \cdot \text{WO}_4 \cdot \text{H}_2\text{O}$, and explodes when rubbed or heated to 80° .

Potassium permolybdate reacts with potash and hydrogen peroxide to form a salt of the composition $\text{K}_2\text{O}_2 \cdot \text{MoO}_4 \cdot \text{H}_2\text{O}_2$, which is a brick-red mass, and explodes spontaneously when preserved in quantity; it loses oxygen and becomes paler when exposed to the air, and evolves oxygen when treated with water. The sodium salt is precipitated as a yellow oil, which decomposes even at -10° , and has not been analysed.

It appears from the foregoing that salts of this kind are less stable as the atomic weight of the metal from which they are produced de-

creases, the salts of permolybdic acid being less stable than those of pertungstic acid, and these again less stable than those of peruranic acid.

A. H.

Action of Iodine on Solutions of Stannous Chloride. By STEWART W. YOUNG and MAXWELL ADAMS (*J. Amer. Chem. Soc.*, 1897, 19, 515—525).—On adding a concentrated solution of stannous chloride (2 mols.) containing hydrochloric acid to iodine (2 mols.), the latter dissolves, and orange-coloured crystals separate, which consist principally of stannic iodide; they contain, however, about 1.25 per cent. of chlorine, which is completely removed on recrystallisation from acetic acid or carbon bisulphide. If an excess of stannous chloride is employed, and the mixture heated with just sufficient water to dissolve the crystals that first separate, orange-red needles are obtained, which consist of stannous iodide contaminated by stannous chloride. The change is, however, not represented quantitatively by the equation $2\text{SnCl}_2 + \text{I}_2 = \text{SnI}_2 + \text{SnCl}_4$; when the proportions are those required by this equation, crystals separate which contain about 5 per cent. of stannous chloride; the latter is present in a still greater proportion when a larger excess of stannous chloride is employed. In such cases, red crystals first separate, but on standing, light-yellow patches of needles are also formed, the composition of which varies; they appear to contain an amount of stannous chloride roughly proportional to the excess of the chloride employed in their preparation, and are probably isomorphous mixtures of stannous iodide and chloride. The amount of the latter varies from 34 to 43 per cent.; and the authors consider that the stannous chloriodide, SnICl , described by Henry (*Phil. Trans.*, 1843, 363), is not a definite compound, but an accidental mixture of stannous chloride and iodide in equivalent proportions.

W. A. D.

Products from an old Cornish Tin Furnace. By WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1897, Nov. 6; and *Amer. J. Sci.*, 1898, [iv], 5, 93—96).—The following crystallised products were obtained from the hearth of an old furnace which had been in use for over 60 years at the Trethellan Tin Works, Truro. The usual Cornish tin ores smelted carried some cobaltiferous mispickel. Most of the crystals are intimately associated with metallic tin.

Stannous Sulphide.—Black, monosymmetric crystals with strong metallic lustre. Iron replaces a little of the tin in the formula SnS .

Iron Arsenide (FeAs).—Dark steel-grey, orthorhombic crystals resembling löllingite in form. Sp. gr. = 7.94.

Iron Arsenide with Stannous Sulphide (FeAs, SnS).—Black, shining, monosymmetric plates, with the same crystal forms as the stannous sulphide mentioned above. In this, and in the iron arsenide, a little cobalt replaces iron.

Tin Arsenide (Sn₆As).—Bright crystals, of a greyish tin-white colour, in the form of six-sided plates. It is soluble in hydrochloric acid with evolution of hydrogen arsenide.

Stannic Oxide.—This, which has been produced by the oxidation of metallic tin, shows the structure of "wood-tin."

L. J. S.

Incandescent Gas Mantles of Commerce. By ERNST HINTZ (*Zeit. anal. Chem.*, 1898, 37, 94—111).—The incandescent mantles in use at the present time consist almost invariably of thoria and of ceria (0·45—2 per cent.), with traces of lime, magnesia, and frequently small quantities of neodymia, yttria, and zirconia. The greatest power of emitting light is exhibited by a mixture of 99 parts of thoria and 1 part of ceria, the emissive power of this mixture being fully ten times as great as that of thoria alone. The substitution of any other of the above rare earths for the ceria tends rather to diminish than to increase the emissive power of thoria, and when present simultaneously with ceria in proportions up to 1 per cent., they in no wise increase the luminous effect. The same is the case with lime (0·5 per cent.), which, moreover, renders the mantles very fragile.

The cerium present may be estimated volumetrically by G. von Knorre's process (*Zeit. angew. Chem.*, 1897, 658, 717), which consists in oxidising the cerium to ceric sulphate by heating with ammonium persulphate and sulphuric acid, then adding a known excess of hydrogen peroxide, by which the ceric salt is reduced to cerous sulphate, and estimating the excess of peroxide by potassium permanganate. A shortened method for estimating the other constituents is also described.

M. J. S.

Separation of Thorium from Cerite Metals. By GRÉGOIRE N. WYROUBOFF and AUGUSTE V. L. VERNEUIL (*Compt. rend.*, 1898, 126, 340—343).—In order to remove thorium from cerium compounds, the latter are reduced to the cerous state, mixed with a small quantity of phosphoric acid, evaporated to a pasty consistency, treated with water, and filtered. All the thorium remains in the precipitate, mixed with some cerium.

To obtain thorium free from cerium, the solution of the nitrates is mixed with an excess of ammonium carbonate, and a small quantity of ammonium hydroxide; all the thorium remains in solution whilst the greater part of the other metals is precipitated. The solution is neutralised as exactly as possible with nitric acid, mixed with excess of hydrogen peroxide, and heated to 60°; all the thorium is precipitated, and if the precipitate is dissolved in nitric acid, evaporated to dryness, redissolved in water, and the treatment with hydrogen peroxide repeated, very pure thorium is obtained. In presence of large quantities of cerite metals, three or four precipitations may be necessary.

The formation of this compound, $\text{Th}_4\text{O}_7\text{N}_2\text{O}_5$, by the action of hydrogen peroxide constitutes a delicate and characteristic test for thorium, and can be used for its quantitative estimation. The oxynitrate cannot, however, be heated or dissolved in acids without loss, and the following method is recommended. The solution of nitrates containing not more than 0·5 gram of oxide is evaporated to dryness, mixed with 100 c.c. of water and 10 c.c. of hydrogen peroxide, heated for a short time, and filtered. The precipitate, after washing, is transferred to a flask and dissolved in hot water containing ammonium iodide and hydrochloric acid, the solution is precipitated with ammonium hydroxide, and the precipitate dried and heated. If the

precipitate of oxynitrate is not white, it must be redissolved in nitric acid, evaporated to dryness, and the process repeated. C. H. B.

Pervanadates. By ANTON SCHEUER (*Zeit. anorg. Chem.*, 1898, 16, 284—304). *Barium pervanadate*, $\text{Ba}(\text{VO}_4)_2$, is obtained as an amorphous, yellow precipitate on adding a solution of barium chloride to a saturated solution of ammonium metavanadate in 30 to 33 per cent. hydrogen peroxide solution, which must be free from sulphuric acid. The product is washed with dilute hydrogen peroxide and dried at the ordinary temperature over calcium chloride. The *potassium salt*, KVO_4 is obtained by dissolving potassium metavanadate in a solution of hydrogen peroxide acidified with sulphuric acid, and is precipitated from the solution as a microcrystalline precipitate by the addition of alcohol; the *sodium salt*, prepared in a similar manner, is very unstable, and cannot be dried without decomposition. The *ammonium*, *lithium*, *strontium*, *calcium*, *lead*, *silver*, and *cadmium* salts are also described; some are amorphous, and others microcrystalline salts of a beautiful bright yellow to deep orange colour.

The author was unable to obtain the corresponding salts of magnesium, aluminium, manganese, cobalt, nickel, or copper.

The acid itself cannot be obtained in a pure state; it is formed on heating ammonium metavanadate, dissolving the brown vanadic acid thus obtained in hydrogen peroxide solution, and evaporating to dryness in a vacuum; a dirty yellow product is thus obtained which dissolves in water with the characteristic red coloration of the pervanadates, and when treated with hydrochloric acid evolves oxygen and chlorine.

Strontium tetravanadate, $\text{SrV}_4\text{O}_{11} + 9\text{H}_2\text{O}$, which formed as a bye-product in the preparation of the pervanadate, crystallises in large, cherry-red crystals from the filtrate after precipitating the latter with alcohol.

Calcium vanadate, $\text{Ca}(\text{VO}_3)_2 + 3\text{H}_2\text{O}$, is obtained in bright yellow needles on adding calcium chloride to a solution of ammonium metavanadate and then precipitating with alcohol.

Manganese vanadate, $\text{Mn}(\text{VO}_3)_2$, is obtained in reddish-brown, six-sided plates by precipitating a solution of ammonium metavanadate with manganese sulphate and boiling the mixture until the amorphous precipitate becomes crystalline. E. C. R.

Antimonic Acids and Antimonates. By A. DELACROIX (*J. pharm.*, 1897, [vi], 6, 337—341. Compare Frémy, *Ann. Chim. Phys.*, 1844, [iii], 12, 499, and 1848, 22, 404; Beilstein and von Bläse, *Abstr.*, 1889, 1123).—Pyrantimonic acid is prepared as follows. Antimony pentachloride is added to 20—25 times its weight of cold water, the excess of chlorine being removed by drawing air through the liquid, and, after remaining for an hour or so, the precipitated hydroxide is transferred to a filter; it is extremely difficult to remove the last traces of hydrogen chloride. When left in contact with cold water, the hydroxide slowly dissolves, yielding a solution of pyrantimonic acid. At 15°, the solution contains 5.88 grams of Sb_2O_5 per litre; at 25°, 8.55 grams; at 60°, 21.30 grams. When treated with mineral acids, a precipitate is obtained, but organic acids have no action. The alkali

hydroxides yield white precipitates soluble in water, but insoluble in an excess of alkali.

When titrated with alkali, using methyl-orange as indicator, neutralisation is reached when the ratio of alkali to Sb_2O_5 is 0.25 : 1. With phenolphthalein, the ratio is 0.5 : 1. The author has not been able to isolate the salt $\text{K}_2\text{O}, 4\text{Sb}_2\text{O}_5$, but the salt $\text{K}_2\text{O}, 2\text{Sb}_2\text{O}_5$ is readily obtained when the acid is treated with a slight excess of potassium hydroxide or acetate. A dilute solution of the acid, when treated with a slight excess of potassium hydroxide and then with much alcohol, yields crystals of the salt KSbO_3 , which gives a characteristic precipitate with sodium salts; the sodium salt, NaSbO_3 , is most readily obtained on adding sodium acetate to a solution of the pyro-acid.

The pyro-acid, when heated for some minutes at 100° , is transformed into the ortho-acid; the same transformation takes place slowly at the ordinary temperature, and the solutions thus obtained are feebly opalescent. The salt KSb_3O_8 , the existence of which was indicated by using methyl-orange as indicator, could not be isolated, but the salt $2\text{K}_2\text{O}, 3\text{Sb}_2\text{O}_5$ is easily prepared; it is less soluble than the normal pyrantimonate.

J. J. S.

Basic Potassium Antimonates. By A. DELACROIX (*J. Pharm.*, 1897, [vi], 6, 533—535. Compare preceding abstract).—The author concludes that Fremy's neutral potassium metantimonate does not exist.

A basic orthantimonate crystallising with $5\text{H}_2\text{O}$ was obtained by treating a 2 to 2.5 per cent. solution of Fremy's gum-like salt with several times its volume of alcohol. After heating at 100° , the crystals contain $3\text{H}_2\text{O}$.

The neutral orthantimonate, $2\text{K}_2\text{O}, 3\text{Sb}_2\text{O}_5$, is obtained when a cold, freshly prepared solution of the so-called granular antimonate is treated with carbonic anhydride. The author thinks that the granular salt and the gum-like salt are both basic potassium orthantimonate.

J. J. S.

Melting Points of Silver and Gold. By DANIEL BERTHELOT (*Compt. rend.*, 1898, 126, 473—476).—The melting points of silver and gold were determined by means of a thermoelectric couple of platinum and platinum-iridium. The values obtained for silver varied between 959.2° and 966.2° with a mean of 962° , whilst those for gold varied between 1062.1° and 1066.70 , with a mean of 1064° . A summary of the results of previous observers is given, and it is noteworthy that, although the absolute values for silver and gold differ with different observers, the interval between the two melting points is in almost all cases about 100° .

C. H. B.

Behaviour of Platinochlorides. By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1898, 16, 305—308. See also this vol., ii, 189).—The author discusses the conditions under which the platinochlorides of the alkalis and alkaline earth are dissociated into the alkali or alkaline earth haloid and platinum chloride; this dissociation appears to be chiefly determined by the temperature. Thus a solution of barium platinochloride deposits crystals of barium chloride at the ordinary temperature, but at temperatures above 80° , barium platinochloride is deposited. The bearing of conditions of the dissociation of platinochlorides on the estimation of potassium is also discussed.

E. C. R.

Mineralogical Chemistry.

Kyanite, Zircon and Anorthite from North Carolina. By JULIUS H. PRATT (*Amer. J. Sci.*, 1898, [iv], 5, 126—128).—Kyanite occurs in decomposed mica-schist near North Toe river, Yancey Co., as large, transparent crystals of a rich grass-green colour; a few are deep blue in the centre with grass-green margins. Sp. gr. = 3·64. No traces of iron or chromium were found. A crystallographic description is given of this kyanite, and also of reddish-brown crystals of zircon from New Stirling, Iredell Co.

The anorthite of a troctolite at Buck Creek, Clay Co., is separated from the olivine by a zone of fibrous silicates, mainly enstatite. The anorthite is somewhat kaolinised, but in the interior is quite free from decomposition. Analysis by C. H. Baskerville of material having sp. gr. = 2·6995—2·7440 gave

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Moisture.	Loss on ignition.	Total.
44·05	30·87	0·84	17·30	0·36	3·65	0·83	0·35	1·60	99·85

L. J. S.

Four New Australian Meteorites. By HENRY A. WARD (*Amer. J. Sci.*, 1898, [iv], 5, 135—140).—*Roebourne*.—This iron was found in 1894 at 200 miles S.E. of Roebourne in N.W. Australia; it measures 57 × 34 × 7 cm., and weighs 86·8 kilos. The Widmanstätten figures are quite regular, but are very dim on account of the great number of small flakes, probably of schreibersite. Troilite nodules are rare. Analysis by Mariner and Hoskins gave I.

Ballinoo.—This was found in 1893 on a tributary of the Murchison River, about 10 miles S. of Ballinoo, in Western Australia; it measures 34 × 27 × 11 cm., and weighs 42·9 kilos. It is an octahedral iron showing very minute Widmanstätten figures. Troilite, schreibersite, and perhaps graphite are present. Analysis II.

Mungindi.—Found in 1897 in Queensland, 3 miles north of Mungindi, P.O., in New South Wales; it measures 39 × 24½ × 17 cm., and weighs 28·1 kilos. A second mass weighs 51 lbs. It is an octahedral iron with well-marked Widmanstätten figures. Troilite and schreibersite are present. Analysis III.

	Fe.	Ni.	Co.	Cu.	Mn.	P.	S.	Si.	C.	Total.	Sp. gr.
I.	90·914	8·330	0·590	—	trace?	0·156	trace	0·010	trace	100·000	7·78
II	89·909	8·850	0·740	trace	—	0·501	trace	trace?	trace	100·000	7·8
III.	90·307	8·230	1·360	—	—	0·093	trace	trace?	0·010	100·000	7·4

Mooranoppin.—Found in or before 1893, near Mooranoppin, 160 miles E. of York in Western Australia. It is an octahedral iron, and the blades of kamacite are so broad that the Widmanstätten figures are not clear. Long fissures in the iron are filled with a black graphitic mineral, and nodules of the same are surrounded by troilite.

L. J. S.

Iron Meteorites as Nodular Structures in Stony Meteorites. By H. L. PRESTON (*Amer. J. Sci.*, 1898, [iv], 5, 62—64).—It is argued that siderites were originally formed and encased in the stony matter of aerolites. It is also pointed out that siderites with a coarsely crystalline structure have rough pitted exteriors, whilst those which are finely crystalline have smooth exteriors. L. J. S.

Physiological Chemistry.

Influence of Bile and Bile Salts on Pancreatic Proteolysis. By RUSSELL H. CHITTENDEN and ALICE H. ALBRO (*Amer. J. Physiol.*, 1898, i, 307—335).—Pancreatic proteolysis, as it occurs in the normal intestine, takes place to a great extent in a neutral or alkaline liquid, and, under such conditions, the proportion of bile ordinarily present is not inimical to the process. If in artificial digestive mixtures of neutral, alkaline, or acid reaction the amount of bile, or bile salts, is increased beyond a certain small proportion, the process of pancreatic proteolysis is hindered. It is believed that the adjuvant power of bile spoken of by previous authors in connection with this process has been much exaggerated, and such small power as bile does possess in this direction is to be attributed to its reaction rather than to the presence of characteristic biliary constituents such as bile salts.

In connection with the reaction of bile, it is pointed out that, although bile is alkaline to litmus, it is acid to phenolphthalein, and that the reaction depends rather on the presence of phosphates than of sodium carbonate.

W. D. H.

Power of Proteids in Conserving Emulsions. By B. MOORE and C. J. I. KRUMBHOLZ (*Proc. physiol. Soc.*, 1898, 54—56).—In conserving emulsions, albumose is practically inert, serum and egg-white nearly so, but acid and alkali albumin, especially the latter, are very effective. The formation of these albuminates during digestion must be of service in the digestion and absorption of fats.

W. D. H.

Nutrition of the Infant. By AXEL JOHANNESSEN and EYVIN WANG (*Zeit. physiol. Chem.*, 1898, 24, 482—510).—A large number of observations (weight, length, composition of the milk given, excretions, including sweat, heat development, &c.) relating to the growth of infants in different parts of the period of lactation.

The authors state they can draw no general conclusions, but present their facts in numerous lengthy tables.

W. D. H.

Formation of Sugar from Fat in the Body. By J. WEISS (*Zeit. physiol. Chem.*, 1898, 24, 542—544).—The following experiment is considered a proof that sugar can be formed from fat in the body.

The blood and liver of rabbits were divided into equal parts; to one half, an emulsion of olive oil, made with gum arabic, was added; to

the other, gum arabic only. The mixtures were kept at 35—40° for 5 to 6 hours, the proteids coagulated by heat and acetic acid and filtered off, the sugar being estimated in the filtrate by Fehling's solution. If blood alone, without liver, was used, the two filtrates contained the same amount of sugar; if the liver was present, the half containing the oil yielded most sugar. The numbers given (sugar per cent.) are as follows.

	With oil.	Without oil.
1.	1·593	1·108
2.	2·542	2·046

With fatty acid, instead of oil, the difference is smaller.

	With fatty acid.	Without fatty acid.
1.	1·343	1·190
2.	2·404	2·100

W. D. H.

[NOTE BY ABTRACTOR.—It seems doubtful whether the experiments described can be considered to prove the author's point.]

Physiology of the Suprarenal Capsule. By SWALE VINCENT (*Proc. physiol. Soc.*, 1898, 48—49, 57—58).—Removal of the suprarenal capsules of the eel, which, as in all teleosts, consist of what corresponds to cortex only of the mammalian gland, is not fatal.

Administration, by the mouth, of suprarenal capsules in large quantities to mammals (rabbits and dogs) produces no results. The active substance of the gland is not destroyed by gastric digestion *in vitro*, so apparently it is not absorbed when taken into the stomach.

W. D. H.

Iodised Fats in the Organism. By HUGO WINTERNITZ (*Zeit. physiol. Chem.*, 1898, 24, 425—448).—The capacity of fats to unite with halogens has been long known, and von Hübl (*Dingler's Poly. J.*, 253, 1884) gives the method for preparing the iodine additive compound. On administering such iodised fats to animals (dogs and birds, given both by the mouth and under the skin), toxic effects were looked for from the possible liberation of iodine; it appears that this is not the case, but that iodised fat is deposited in the organism, principally in the adipose tissue, but also in the fat of the bones, muscles, and liver, whilst traces pass into the milk. In artificial digestion experiments, the alkaline juices were found to liberate some iodine, whilst the gastric juice did not. The excretion of iodine in the urine continues for 10 days after the feeding is stopped.

The administration of potassium iodide does not lead to the formation of iodised fat in the body, except that traces were found in the mammary glands, bone, marrow (in hens), and in the hair.

W. D. H.

Behaviour of different Sugars after Subcutaneous Injection in Man. By FRITZ VOIT (*Chem. Centr.*, 1897, ii, 867—868; from *Deutsch. Arch. Klin. Med.*, 58, 523—564. Compare Abstr., 1897, ii, 511).—Dextrose, levulose, and galactose are decomposed by the body cells, whereas sorbinose is recoverable in the urine. The pentoses

(arabinose, xylose, and rhamnose) are only partially destroyed, and appear in great measure in the urine; the same occurs when they are given by the mouth. Cane-sugar and lactose appear almost quantitatively in the urine, and so contrast with maltose. In the case of trehalose, 15 to 17 per cent. of the amount injected was recovered in the urine; raffinose is also largely excreted in the same way. Glycogen is neither excreted as such nor as sugar; 34 per cent. of the achroo-dextrin prepared by diastase, 24 per cent. of that prepared by acid, 14 per cent. of erythro-dextrin, and 28 per cent. of amylo-dextrin (excreted as achroo-dextrin) were recoverable in the urine. In these cases, no sugar was found in the urine. W. D. H.

Stercorin. By STANISLAS BONDZYŃSKI and V. HUMNICKI (*Zeit. physiol. Chem.*, 1898, 24, 395—398).—Flint states (*Abstr.*, 1897, ii, 575) that the substance koprosterol described by the authors is the same as that which he described under the name stercorin many years ago. This is disputed, and Marcet's *excretin* is regarded as nearer to koprosterol than stercorin, although Marcet did not recognise the possibility of its origin from cholesterol. W. D. H.

Intestinal Epithelium and Absorption. By E. WAYMOUTH REID (*Proc. physiol. Soc.*, 1898, 56—57).—The absorption of serum in loops of intestines in living dogs was investigated. Both water and solids are taken up by the intestinal wall when the hydrostatic pressure in the gut is well below that in the capillaries of the villi. The inorganic salts are absorbed rather more quickly than the water, the organic solids more slowly.

Removal of the epithelium by temporary ligature of the vessels, or by washing with distilled water, or poisoning of the epithelium by sodium fluoride, reduces or stops the absorption. W. D. H.

Excretion of Nitrogenous Substances in Diabetes Mellitus. By MARTIN JACOBY (*Chem. Centr.*, 1897, ii, 528; from *Zeit. klin. Med.*, 32, 556—568).—In cases of diabetes mellitus, the ratio of total nitrogen to the nitrogen of alloxuric substances varies, with the severity of the case, from 24·9 to 38·7:1; the absolute value of the total alloxuric substances being between 0·29 and 1·03 grams. In a case of *diabetes insipidus*, the two numbers were respectively 18·6:1 and 0·57 grams. W. D. H.

Phloridzin-Diabetes in Dogs. By F. H. REILLY, F. W. NOLAN, and GRAHAM LUSK (*Amer. J. Physiol.*, 1898, i, 395—410).—Frequent subcutaneous injections of phloridzin in fasting dogs establish ultimately the ratio in the urine of dextrose:nitrogen = 3·75:1, which indicates a production of 60 grams of dextrose from 100 grams of proteid. Taking the fæcal nitrogen into account, the amount of dextrose obtainable from proteid may be more accurately estimated at 58·7 per cent.

The proteid metabolism may increase above that in simple fasting to an extent as high even as 560 per cent.

Dextrose given during phloridzin-diabetes is quantitatively eliminated; levulose and galactose are not eliminated as such, but only in so far as they are converted into dextrose. The administration of

fat does not affect the ratio ; the giving of meat also does not affect the ratio for the day, but the sugar from the proteid eaten may be eliminated before the nitrogen belonging to it, on account of an early preliminary cleavage of the molecule.

Gelatin yields the same amount of sugar as proteid, and spares much proteid from metabolism.

Intestinal putrefaction and fermentation can only have slightly affected the proteid or dextrose given in these experiments.

W. D. H.

A Case of Poisoning by Hydrogen Arsenide. By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1898, **24**, 511—512).—The urine in the case described was abundant, and contained hæmoglobin, albumin (1 per cent.), and urobilin. Bile acids and salts were absent. Traces of arsenic were found.

W. D. H.

Physiological Action of Aldehyde, Salicylaldoxime, and Acetoxime. By ORAZIO MODICA (*Chem. Centr.*, 1897, ii, 500 ; from *Ann. Chim. Farm.*, **26**, 289—301).—In dogs and frogs, salicylaldehyde produces chiefly paralysis, whilst its oxime stimulates, and only paralyzes in large doses. In opposition to the observations of Curci, it is found that, after the administration of acetoxime, acetone is found in the urine, and the physiological action of acetoxime is probably due to the acetone liberated.

W. D. H.

Physiological Action of Cotarnine. By PIO MARFORI (*Chem. Centr.*, 1897, ii, 368, from *Ann. Chim. Farm.*, **25**, 241—251).—Cotarnine or stypticine differs from hydrastinine by containing the group OMe in place of a hydrogen atom. The present research is to ascertain whether its styptic properties are due, like those of hydrastinine, to its vaso-constrictive properties. This is not the case, nor does it act by hastening the coagulation of the blood. In the central nervous system, there is first stimulation and then paralysis.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation without Cells. By EDUARD BUCHNER (*Ber.*, 1898, 31, 568—574).—An account of a lecture delivered to the German Chemical Society. Fresh bottom-fermentation yeast from a Munich brewery, compressed under 50 atmos. pressure to remove water, is pounded in a porcelain mortar by mechanical power, after mixture with an equal weight of quartz sand and one-fifth of its weight of kieselguhr; by this treatment, 40 per cent. of the yeast cells are disintegrated. The mass, which has now become pasty, is subjected to a pressure of 500 atmos. in a hydraulic press, the expressed juice being allowed to fall on to a fluted paper filter, and collected in a vessel kept cool with ice; after 2 hours, the cake is broken up, moistened with water, and again pressed. From 1 kilo. of yeast, 500 c.c. of extract is

obtained, although only 140 c.c. water has been added. The residual cake has now but little power of inducing fermentation; in it only 4 per cent of the yeast cells are intact, and of about 60 per cent. nothing but empty cell-walls remain.

This extract contains *invertin*, a *maltase*, and a *ferment* capable of hydrolysing glycogen. Further, it appears to contain an *oxydase*, for it turns brown after long exposure to the air; it also contains a *proteolytic enzyme*, for, although the fresh extract coagulates when heated to 50°, it no longer does this after it has been allowed to remain for a week at the ordinary temperature. Most important of all, it ferments sugar to alcohol and carbonic anhydride, and this no less rapidly than fresh yeast does; the agent of the change may be named *zymase*. 200 c.c. of the extract, freed from dissolved carbonic anhydride by exposure under diminished pressure, is mixed with sugar to a concentration of 16 per cent., and 2 per cent. of potassium metarsenite added. This mixture gave 15 grams of carbonic anhydride by the time it had stood 40 hours at 15°; all the sugar (33.4 grams) had disappeared, and 15 grams of alcohol were obtained. The fermentation cannot be induced by the few micro-organisms present; it is too rapid for that, and, moreover, the extract induces fermentation even after it has been freed completely from organisms by filtration. Further, it cannot be due to the action of living protoplasm present in the extract, for it is not hindered by the presence of arsenious acid, chloroform, benzene, or large quantities of glycerol or sugar. The fermentation has exactly the character of the ordinary fermentation with yeast, alcohol and carbonic anhydride being formed in about equal amounts; cane-sugar, maltose, grape-sugar, and levulose are fermented, lactose and mannitol are not.

There is never absolute certainty that *zymase* will be present in the extract from a given sample of yeast; occasionally it is absent without apparent reason.

C. F. B.

Oxydase of Grapes; its Utility in Wine-making. By A. BOUFFARD and L. SEMICHON (*Compt. rend.*, 1898, 126, 423—426).—The preparation of white wines from purple grapes is readily effected by taking advantage of the presence of an oxydase in the grape juice. A current of air, as finely divided as possible, is passed into the must, and through the medium of the ferment the colouring matter is thereby oxidised and consequently precipitated. The point at which complete precipitation of the colouring matter has been effected is readily ascertained by filtering some of the must, which should, of course, be colourless. Prolonged passage of the current of air is to be avoided, since it tends to make the wine yellow and then brown.

The oxydase is present chiefly in the vascular tissue of the grapes, and they should be subjected to moderately heavy crushing, in order that the proportion of the oxydase in the must may be sufficient, but not much more than sufficient, to promote fairly rapid precipitation of the colouring matter. If any oxydase is left in the wine after fermentation, it tends to produce an injurious yellow colour, and consequently it is advisable to destroy the oxydase by adding a small quantity of sulphurous acid in the form of potassium hydrogen

sulphite, 2 to 5 grams per hectolitre being sufficient. A similar addition is advisable in the case of white wines prepared from white grapes, and also in the case of pale wines. In the manufacture of red wines, it is important that the grapes should be crushed carefully, so that the proportion of oxydase in the must may be as low as possible, otherwise too much of the colouring matter may be precipitated.

When all the colouring matter has been precipitated with a view to the preparation of white wine, it is not necessary to remove the precipitate before fermenting the must in the usual way. C. H. B.

Oxidation of Compound Ammonias by Ferments in Soils. By E. DEMOUSSY (*Compt. rend.*, 1898, 126, 253—256).—Experiments were undertaken with a view to throw light on the changes experienced in soils by organic matter of the nature of amines. The compounds investigated were placed in flasks containing water, calcium carbonate, and potassium phosphate, sterilised, mixed with some garden soil, and kept at 30°. Methylamine, in the form of sulphate, is completely converted into ammonia after some days, and subsequently, but not before, nitrites and nitrates are formed. The change does not take place in the absence of soil, nor in the absence of calcium carbonate. No change takes place in a vacuum, and the presence of oxygen is essential, which indicates that the alkyl radicle is oxidised. Trimethylamine is oxidised much more slowly, but the change is direct, and the three methyl groups are attacked simultaneously, no methylamine being formed as an intermediate product. Aniline is oxidised very slowly, and pyridine still more slowly, whilst quinoline yields traces of ammonia only after several months, oxidation being more difficult the more complex the molecule. C. H. B.

Nitrification Bacteria. By ALBERT STUTZER and R. HARTLEB (*Chem. Centr.*, 1897, ii, 502; from *Centr.-Bl. f. Bakt. u. Parasitenk.*, 3, ii, 311—321. Compare this vol., ii, 301 and 302).—The organisms which bring about nitrification are able to obtain carbon from the carbonic anhydride of the atmosphere or from soluble carbonates. They are unable, however, to assimilate the carbonic anhydride of calcium carbonate, just as Godlewski showed was the case with magnesium carbonate, provided the culture liquids contain no carbonic anhydride, and the culture is kept in an atmosphere free from this gas. It does not follow, however, that the natural carbonates, which are insoluble in water, are not of use to the organism, for carbonic anhydride is always being liberated by the action of the acids formed by the oxidation of nitrogenous compounds in the process of nitrification.

The presence of even small quantities of glycerol enables the organism to obtain carbon, and to form nitrate from nitrite, and when larger quantities are present the organism becomes more highly developed, forming thread-like bacteria with mycelium filaments. When a culture well supplied with carbon in the form of glycerol or similar substance, and of nitrogen in the form of nitrite, is kept deprived of atmospheric oxygen, the organism obtains its oxygen from the nitrite, and nitrogen is liberated. Bicarbonates are good nutritive materials, and enable the organism to oxidise nitrites, although only

when supplied with oxygen; the organism may, however, live for a long time when deprived of free oxygen, but is then quite inactive. Ammonium carbonate is an unsuitable source of carbon. As the culture, which consists of a solution of gelatin in potable water containing potassium phosphate, becomes exhausted, the mycelium threads, the micrococci and the spore-tubes become smaller, and nitrates are only formed when the culture begins to be poor in assimilable carbon, and the whole of the soluble organic nitrogen compounds are oxidised to nitrite. At this stage, nitrification is effected by the micrococci and bacilli. The production of nitrite is not associated with organisms of any particular shape, for this depends on the material in which they are cultivated.

The nitrifying organisms found in the soil of the Cameroons are physiologically and morphologically identical with those of German soil.

E. W. W.

New Method of Disinfection. By REINHOLD WALTHER and ARTHUR SCHLOSSMAN (*J. pr. Chem.*, 1898, 57, 173—197).—After a lengthy review of all the known methods of disinfection, the authors state that by far the best results are obtained by using a solution of formaldehyde in glycerol, which they call “glycoformal.” This is dispersed through the room to be disinfected in the form of a very fine mist, half an hour sufficing to absolutely destroy all germs. Details of the method will be published on another occasion.

A. W. C.

Analytical Chemistry.

Methods of Gas Analysis. By JOHN S. HALDANE (*J. Physiol.*, 1898, 22, 465—480).—Some forms of gas-burettes and other details in the methods used by the author in his work on the gases of the air and blood, are described and figured. W. D. H.

Separation and Estimation of Bromine, Chlorine, and Iodine. By ADOLPHE CARNOT (*Compt. rend.*, 1898, 126, 187—191).—Iodine is liberated by adding a solution of nitrogen oxides in sulphuric acid, separated by means of carbon bisulphide, and estimated by titration with sodium thiosulphate, after washing the bisulphide solution with water. In the same liquid, the bromine, liberated by adding sulphuric and chromic acids and heating at 100°, is separated by means of carbon bisulphide, and estimated by adding excess of potassium iodide to the bisulphide solution (after washing), and then titrating with thiosulphate. After removal of the iodine and bromine, chlorine is estimated either by precipitation or volumetrically. The total halogens may also be determined gravimetrically or volumetrically in a separate portion of the liquid, the chlorine being afterwards estimated by difference.

The separation of the iodine and bromine is best conducted in a

separating funnel with a well-fitting stopcock, closed at the top with a glass stopper. The glass should be thin, so that the funnel may be floated in water at 100° to ensure complete liberation of the bromine.

C. H. B.

Estimation of Sulphur in Iron. By LOUIS CAMPREDON (*Chem. Centr.*, 1897, ii, 383; from *Stahl und Eisen*, 17, 486—489).—The author thinks that Schulte (this vol., ii, 45) is wrong in supposing that iron, when treated with hydrochloric acid, yields all its sulphur as hydrogen sulphide. Sometimes only one-half of the sulphur is obtained in that form, the remainder being evolved in other gaseous forms, which, however, are converted into hydrogen sulphide when passed through a red-hot glass tube.

The best solvent for iron is a mixture of 2 parts of dilute hydrochloric acid (1:2) and one part of dilute sulphuric acid (1:4).

L. DE K.

Estimation of Sulphur in Iron. By WILHELM SCHULTE (*Chem. Centr.*, 1897, ii, 383; from *Stahl und Eisen*, 17, 489—493).—The author, in reply to Campredon (see preceding abstract), states that he is well aware of the fact that a considerable part of the sulphur is not evolved as hydrogen sulphide. The apparatus should be previously filled with carbonic anhydride and the gases passed through a combustion tube 15—20 cm. long heated to dull redness.

L. DE K.

Estimation of Carbon, Nitrogen, and Halogens by means of Alkali Persulphates. By HEINRICH BRUNNER (*Chem. Centr.*, 1897, ii, 389; from *Schweitz. Wochschr. Pharm.*, 35, 280—281).—The author has previously shown that organic carbon is completely oxidised by means of potassium persulphate mixed with potassium permanganate. The nitrogen is liberated as such, but in the presence of a sufficient amount of alkali, it is completely converted into ammonia. The process is also applicable to the estimation of the halogens; chloral, for example, when heated with potassium persulphate, yields free chlorine which may be collected in an absorption apparatus containing potassium iodide solution.

L. DE K.

Estimation of Nitrogen in Manures. By ARTHUR DEVARDA (*Chem. Centr.*, 1897, ii, 64—65; from *Österr.-ungar. Zeit. Zucker-Ind.*, 1897).—A quantity of the sample which should contain not more than 0.4 gram of saltpetre is dissolved in 150 c.c. of water and 8 c.c. of aqueous potash of sp. gr. = 1.3, and 1.5 grams of an aluminium alloy containing 59 per cent. Al, 39 of copper and 2 of zinc is added. The flask is at once connected with a suitable distillation apparatus, and after half an hour the ammonia is distilled off and titrated. To obtain the remainder of the nitrogen, 25 c.c. of strong sulphuric acid and half a gram of mercury are added and the process continued as in Kjeldahl's method.

L. DE K.

Estimation of Phosphorus in Phosphides. By LÉON FRANCK (*Zeit. anal. Chem.*, 1898, 37, 173—176).—The following method was devised for the estimation of the phosphorus in aluminium phosphide,

a substance which is decomposed by water, acids, and alkalis, with evolution of hydrogen phosphide. A flask is fitted with a separating bulb, through which carbonic anhydride from a Kipp's apparatus can be introduced. An evolution tube (carrying a Bunsen's valve to prevent regurgitation) connects the flask with a series of three absorption vessels (Blum's) containing respectively 20, 20, and 15 c.c. of hydrochloric acid saturated with bromine. Having filled the whole apparatus with carbonic anhydride, the substance (0.3–0.4 gram), weighed in a stoppered tube, is introduced into the dry flask, and carbonic anhydride again passed through; 50 c.c. of water, followed by 50 c.c. of dilute sulphuric acid (1:2), is then slowly dropped in. After half an hour's repose, the contents of the flask are boiled for half an hour, and the last traces of gas are swept out by carbonic anhydride. The hydrogen phosphide is completely absorbed by the bromine, and oxidised to phosphoric acid, which, after evaporating the contents of the absorption vessels to dryness on the water bath, is estimated by the usual processes. A blank experiment is advisable for ascertaining the purity of the reagents. An attempt to substitute dilute nitric acid for the sulphuric acid resulted in a violent explosion.

M. J. S.

Estimation of Phosphorus in Steel and Iron. By LEOPOLD SCHNEIDER (*Chem. Centr.*, 1897, ii, 385; from *Österr. Zeit. Berg-Hütt.*, 45, 326–328).—This paper deals with the various modifications of the molybdate method. As the phosphorus is not completely oxidised by nitric acid alone, the oxidation must be completed with potassium permanganate, the excess of the latter being removed by oxalic or tartaric acid, or ferrous sulphate. The precipitation is best effected by means of a strongly acid solution, containing much ammonium nitrate; and if time is no object, the operation is best carried out in the cold, so as to avoid precipitation of molybdic acid. The yellow precipitate may be very conveniently treated, according to Pinkener's directions, namely, by gently igniting it, when it will contain 1.65 per cent. of phosphorus. The volumetric estimations based on the reduction of the molybdic acid are not recommended. Silicon does not interfere, but arsenic and tungstic acids should be first removed.

L. DE K.

Estimation of Small Amounts of Phosphoric Acid. By ADOLF JOLLES and FRIEDRICH NEURATH (*Monatsh.*, 1898, 19, 5–15).—When the yellow precipitate obtained by the action of ammonium molybdate on a phosphate is dissolved in ammonia, and the solution evaporated, a white salt of the composition $(\text{NH}_4)_3\text{PO}_4 \cdot 5(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, is obtained, which is characterised by giving delicate colour reactions with salts of the heavy metals, and a yellow colour with many organic acids, although not with hydroxy-acids. The authors propose the following method for the estimation of small amounts of phosphoric acid. The solution to be tested is first precipitated with ammonium molybdate, and the precipitate dissolved in ammonia, and evaporated; the phosphoric acid is then determined by comparing the intensity of the bluish-green colour produced by ferrous sulphate, with that produced in a solution of phosphomolybdate containing a

known amount of phosphoric acid. By this reaction, as little as 0.00004 gram P_2O_5 can be detected in 20 c.c. of water.

A second method is based on the fact that phosphoric acid gives only a yellow coloration with sodium or potassium molybdate, the intensity of which increases with the temperature. The following is the procedure:—20 c.c. of the solution to be tested is placed in a test-tube, and, in a second tube, 20 c.c. of a solution in which the amount of phosphoric acid is known. A similar quantity of sodium molybdate is then added to each, and the colours compared. The reaction, which detects as little as 0.000025 gram P_2O_5 in 20 c.c. of water in the cold, and 0.0000025 gram on warming, is not hindered by the presence of other inorganic salts.

A. W. C.

Estimation of Boric Acid in Meat. By C. FRESENIUS and GEORG POPP (*Chem. Centr.*, 1897, ii, 69; from *Zeit. öffentl. Chem.*, 3, 188—190).—Ten grams of the chopped meat is triturated in a mortar with 40 to 80 grams of anhydrous sodium sulphate, and dried in the water oven; the mass is then finely powdered, if necessary, with the addition of more sodium sulphate, introduced into a 300 c.c. Erlenmeyer flask, and 100 c.c. of methylic alcohol added. After standing for 12 hours, the alcohol is distilled off; 50 c.c. more methylic alcohol is poured on to the residue, and this is again distilled off. The distillate is finally made up with methylic alcohol to 150 c.c., and 50 c.c. of this is mixed with 50 c.c. of water and 50 c.c. of 50 per cent. glycerol solution containing phenolphthalein, and carefully neutralised with soda; after thoroughly mixing the liquid, it is carefully titrated with N/20 soda solution, 1 c.c. of soda = 0.0031 gram of crystallised boric acid. Another portion of the alcoholic distillate may be ignited, when, if boric acid be present, the characteristic green flame will be noticed.

The exhausted meat may be incinerated, and the ash tested for borates.

L. DE K.

Gas-Volumetric Estimation of Carbon in Iron and Steel. By EDUARD DONATH and W. EHRENHOFER (*Chem. Centr.*, 1897, ii, 61—62; from *Österr. Zeit. Berg.-Hütt.*, 45, 284—286).—The apparatus is a modification of the one recommended by Wiborgh. According to the supposed richness in carbon, 0.2 to 4 grams of the sample is treated with 10 times its weight of a saturated solution of copper sulphate, and the spongy mass is then oxidised by heating with sulphuric acid previously diluted with one-fifth of its bulk of water and a sufficiency of chromic acid. The volume of the gases given off is measured, and the carbonic anhydride found by absorption.

L. DE K.

Estimation of Carbonic Anhydride in the Air. By W. LEWASCHEW (*Chem. Centr.*, 1897, ii, 67—68; from *Hyg. Rundsch.*, 7, 433—437).—The process is based on the same principle as the well-known Pettenkofer's method, in so far as baryta-water is titrated with oxalic acid, before and after exposure to the sample of air.

The baryta-water is contained in a 100 c.c. flask, fitted with a perforated indiarubber cork closed by a glass rod. After removing the rod, the flask is inverted and its neck pushed into the perforated indiarubber

cork fitted to a 6 litre flask, which has been previously filled with the suspected air by means of a pair of bellows. By reversing the flask, the baryta-water runs back into the small flask, and can be titrated.

L. DE K.

Colorimetric Estimation of the Denseness of Smoke. By P. FRITZSCHE (*Zeit. anal. Chem.*, 1898, 37, 92—94).—A known volume of the flue gases (10—20 litres) is aspirated through a cotton wool filter. The latter, after using its cleaner portion for wiping out the tubes, is shaken vigorously with 200 c.c. of water in a stoppered bottle, and the greyish liquid is poured into a test tube 40—50 mm. in diameter. The depth of colour is then compared with a scale of paper discs tinted with Indian ink, which have been standardised once for all, by comparison with known weights of soot shaken up with water and cotton wool exactly as above.

M. J. S.

Detection of Traces of [Normal] Alkali Carbonates in the Presence of an Excess of Acid Carbonate or of Borax. By ALEX. LEYS (*J. pharm.*, 1897, [vi], 6, 440—442).—Large quantities of acid carbonates or of borax prevent the formation of a precipitate when an alkali carbonate is mixed with magnesium sulphate. A delicate test for small quantities of normal alkali carbonates in the presence of bicarbonates or borax is a saturated solution of calcium sulphate. Even traces of a normal carbonate give an immediate precipitate, whereas a pure bicarbonate gives a crystalline precipitate only after some time, and borax gives no precipitate.

J. J. S.

Analysis of Bar Copper. By WILHELM HAMPE (*Chem. Centr.*, 1897, ii, 222—223, 391, 811—812; from *Berg.-Hüttenm. Zeit.*, 56, 145—147, 201—203, 297—299).—A reply to Murmann (*Abstr.*, 1897, ii, 346), who objects to the author's process for estimating oxygen in bar copper.

Copper filings should be used, and these should be boiled for a few seconds in weak aqueous potash to dissolve any greasy matter present. The metal is then washed, first with water and subsequently with absolute alcohol.

The author does not agree with Murmann, who has stated that foreign oxides are not so readily reduced by hydrogen as cuprous oxide. To estimate the latter, the metal foil is treated with excess of a 6 per cent. solution of silver nitrate, which dissolves the metallic copper completely, but only one-third of the cuprous oxide. The precipitate, consisting of metallic silver and basic copper nitrate, is then dissolved in dilute nitric acid, and the solution freed from silver by cautiously adding hydrochloric acid; any copper is estimated in the filtrate.

If it is desired to estimate the metallic copper directly, a large quantity, say 50 grams, of the sample may be taken, and the copper precipitated by electrolysis. It is, however, advisable to stop the current before the metal has been completely deposited; the last portions of copper are then precipitated from the solution and weighed as sulphide.

L. DE K.

[Volumetric Estimation of Cerium.] By ERNST HINTZ (*Zeit. anal. Chem.*, 1898, 37, 94—111).—See this vol., ii, 339.

Assay of Nickel-Copper Alloys. By ALFRED RICHE (*Journ. Pharm.* 1897, [vi], 6, 300—303).—The nitric acid solution of the alloy is twice evaporated to dryness with a few drops of sulphuric acid, and the copper estimated by the usual electrolytic method. The solution from which the copper has been deposited is then treated with an excess of ammonia and the nickel deposited electrolytically by the aid of three Daniell's cells.
J. J. S.

Electrolytic Estimation of Manganese and the Separation of Iron from Manganese. By FRIEDRICH KAEPEL (*Zeit. anorg. Chem.*, 1898, 16, 268—283).—A dense deposit of manganese peroxide which is not easily separated from the electrode, is obtained by adding acetone to the electrolyte. The manganese sulphate solution, contained in a platinum dish, is maintained at 50—55°, great care being taken that the dish is evenly heated and that the temperature remains constant: with a current of 0.7 to 1.2 ampères and a potential difference of 4—4.25 volts, from 0.15 to 1.6 grams of manganese peroxide is deposited in 2 to 5½ hours. To obtain a good deposit requires the addition of 1.5 to 10 grams of acetone, according to the amount of manganese present. About 150 c.c. of manganese solution is employed, and during the electrolysis the volume must be kept constant by allowing water to drop into the platinum dish from a dropping funnel. The deposit of manganese peroxide is washed without breaking the current, dried at 150 to 180°, and weighed as anhydrous peroxide. The results which the author obtained are accurate.

The estimation of iron in the presence of manganese is most advantageously carried out as follows. The solution of iron and manganese sulphates is poured into a boiling solution of sodium pyrophosphate, employing about 12 grams of the pyrophosphate for about 0.15 gram of iron; after a clear solution is obtained, 3 to 4 drops of phosphoric acid are added, and if this causes a turbidity, sodium pyrophosphate is added until the solution becomes clear. During the electrolysis, the solution is kept at 30—40°, and, with a current of 1.8 to 2.5 ampères, the electrolysis is complete in 8—9 hours. The deposit of metallic iron, which adheres well to the platinum dish, is washed without breaking the current, and afterwards washed with absolute alcohol and dried at a low temperature. The results are fairly accurate, being about 0.15 per cent. too low.
E. C. R.

Estimation of Hydrogen Cyanide in Ethereal Oil of Bitter Almonds. By F. DIETZE and by ANTON (*Zeit. anal. Chem.*, 1898, 37, 204; from *Zeit. Allegem. österr. Apoth.-Vereins*, 50, 942).—According to Dietze, *Oleum amygdalarum aethereum* should contain between 1.5 and 2 per cent of hydrocyanic acid. Anton gives the following modification of Vielhaber's method:—2 grams of the substance is mixed with 10 grams of magnesium hydroxide, 10 c.c. of water, and a few drops of potassium chromate solution, and is titrated with N/10 silver nitrate, exactly like a chloride. 1 c.c. = 0.0027 gram of HCN.

M. J. S.

Volumetric Estimation of Zinc and Manganese. By GEORGE C. STONE and D. A. VAN INGEN, and by EDMUND H. MILLER and JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1897, 19, 542—547 and 547—558). See this vol., i. 347, 348.

Estimation of Phenols in Ethereal Oils. By EDWARD KREMERS and OSWALD SCHREINER (*Chem. Centr.*, 1897, ii, 147—148; from *Pharm. Rev.*).—To estimate thymol, the following process is recommended. A known weight of the sample is mixed in a glass-stoppered burette with an equal volume of light petroleum, and after carefully noting the volume, it is agitated with 5 per cent. aqueous potash and the alkaline layer is drawn off into a graduated 10 c.c. measure, the operation being repeated several times until no further diminution of the oily layer takes place. To make sure that all the thymol has been removed, a drop of the oil is dissolved in 20 drops of chloroform and gently warmed with a small piece of sodium hydroxide. If thymol is present, the liquid turns red.

The alkaline liquid is then made up to a definite bulk, and the thymol titrated in an aliquot part with N/10 iodine solution in the usual manner; it appears that the results obtained by titration are about 3 per cent. lower than the decrease in volume. Other phenolic compounds are similarly estimated.

L. DE K.

Discrimination of Guaiacol and Creosote. By S. VREVEN (*Zeit. anal. Chem.*, 1898, 37, 132; from *Mon. Pharm.*, 1896, 549).—To a drop of the liquid in a test-tube 2—3 drops of ether and one or two drops of concentrated nitric and hydrochloric acids are added, and the mixture is shaken, when it acquires a brownish-red colour.

On spontaneous evaporation of the ether, guaiacol yields needle-shaped crystals, whilst creosote produces only oily drops. Phenol gives a similar reaction, but the crystals are easily distinguished from those of guaiacol.

M. J. S.

New Method of Estimating Sugar. By KARL B. LEHMANN (*Chem. Centr.*, 1897, ii, 233; from *Pharm. Post.*, 30, 331).—A measured quantity of Fehling's solution containing a known weight of copper is mixed with a known volume of sugar solution and boiled until the reduction is complete. The liquid is then made up to a definite bulk, and when the cuprous oxide has subsided, an aliquot part of the liquid is pipetted off.

After adding a slight excess of sulphuric acid, the excess of copper is titrated in the well-known way with potassium iodide and sodium thiosulphate, using starch as indicator.

L. DE K.

Technical Estimation of Invert-Sugar by Peška's Method. By K. ANDRLÍK (*Chem. Centr.*, 1897, ii, 393—394; from *Zeit. Zuck. Ind. Böhm.*, 21, 569—583).—The solution is clarified with basic lead acetate, the excess of lead removed with sodium sulphate or phosphate, the filtrate examined polarimetrically, and then diluted to such an extent that 100 c.c. contain 2.5 grams of sucrose. The liquid is then treated for invert-sugar by means of Peška's ammoniacal copper solution. Tables and curves are given in the original paper.

L. DE K.

Estimation of Sugar and the Polarimetric Examination of Sweet Wines. By ARTHUR BORNTÄGER (*Zeit. anal. Chem.*, 1898, 37, 145—172).—The wine is accurately neutralised with an alkali hydroxide, at first in the cold, but heating as the end is approached, then evaporated on the water bath to about half its volume (but not to a syrup); decolorised, after cooling, with a "moderate" amount of basic lead acetate (the meaning of which seems to be that the excess should be as small as possible), made up to its original volume, and filtered through dry paper. After not less than 12 hours, the liquid, which must be neutral or feebly acid, is fit for both optical examination and titration by the Fehling-Soxhlet method. To detect and estimate saccharose, the wine, mixed with one-tenth of its volume of hydrochloric acid of sp. gr. = 1.1, is heated for 15 minutes at 65—70°, then neutralised and treated as before, the presence of saccharose being indicated by an increase of lævorotation, and its amount calculated from the increase in the reducing power. In justification of the above mode of procedure, the author has investigated the influence of the several operations and conditions (compare this vol., ii, 264), and shows, both from his own experiments and those of others, (1) that both dextrose and levulose undergo a transient diminution of rotatory power when their solutions are evaporated or even heated; (2) that whilst the presence of basic lead acetate diverts the optical rotation of invert-sugar towards the right, neutral or acid lead solutions are absolutely without influence; (3) that the volume of the lead precipitate may be neglected without sensible error, or, at most, only compensates for the precipitation of a trace of invert-sugar by the basic lead acetate; (4) that the optical and chemical properties of invert-sugar are not affected by prolonged contact with normal lead acetate; (5) that no error results from the limited evaporation of the neutralised wine; (6) that the presence of much lævorotatory sugar does not prevent the detection of small quantities of saccharose; (7) that the removal of the alcohol by evaporation is essential; (8) that precipitation of the excess of lead by sodium carbonate, as prescribed in the official German and Italian methods, is a source of error, since the rotation of an invert-sugar solution is increased by the presence of soda; sodium sulphate and phosphate seem free from this objection.

M. J. S.

Detection of Carbohydrates. By B. SJOLLEMA (*Chem. Zeit.*, 1897, 21, 739).—The reagents consist of a 10 per cent. solution of cupric sulphate to which an excess of ammonia has been added just sufficient to redissolve the precipitate, and a 5 per cent. solution of cupric acetate containing a little free acetic acid which has been treated with ammonia in the same way as the sulphate. Two c.c. of the sugar solution is mixed with 0.5 c.c. of the reagent. The sulphate solution is a delicate test for glucose, yielding a voluminous precipitate with a solution containing 0.5 per cent. or even less of this sugar; for the detection of levulose, the acetate should be employed. The presence of saccharose does not interfere. Lactose and galactose also give insoluble copper compounds; to detect galactose, the acetate solution should

be used, as the sulphate is not very suitable for either lactose or galactose. Excess of ammonia interferes with the lactose reaction more than it does with the hexoses. The author has not yet tried the behaviour of mannose and maltose towards ammoniacal copper solutions.

L. DE K.

Methods of Estimating the Quality of Flour. By VICTOR VEDRÖDI (*Zeit. anal. Chem.*, 1898, 37, 87—92).—In 1893 (*Zeit. angew. Chem.*, 691) the author proposed to distinguish the different grades of flour by the estimation of the ash, on the ground that the larger the amount of bran in the flour the higher will be the percentage of ash; and the following limits were laid down.

No.	0	1	2	3	4	5	6	7	8
Limits of percentage of ash.	{ 0.24	0.35	0.40	0.44	0.53	0.61	0.71	1.17	1.81
	{ 0.34	0.39	0.43	0.52	0.60	0.70	1.16	1.80	3.15

To this it was objected by Cerkez (*ibid.*, 1895, 663) that the method would operate prejudicially against mill employing mill-stones, since the introduction of a few hundredths per cent. of mineral matter abraded from the stones would suffice to lower the apparent quality of the flour by several grades, and it was proposed to adopt the percentage of oil as the criterion of quality, the limits laid down being as follows.

No.	0	1	2	3	4	5	6	7	8
Limits of percentage of oil.	{ 0.60	0.96	1.06	1.16	1.26	1.46	1.63	1.85	2.51
	{ 0.95	1.05	1.15	1.25	1.45	1.62	1.84	2.50	3.45

The author has now estimated both the oil and ash in 56 samples of flour from mills employing both steel rollers and mill-stones, and has compared the grades indicated by the determinations, with those assigned by the millers on the basis of eye estimations. The latter agree with Cerkez's numbers in only 19 cases, whilst in 40 cases they agree with the numbers deduced from the ash determinations. Where differences exist, they are of greater magnitude with the former method than with the latter, and the fact that the ash method, when it differs from the eye estimation, usually assigns the higher value to the flour is a proof that the objection advanced by Cerkez is groundless. The ash estimations were all made by incinerating 5 grams of flour in porcelain crucibles in a muffle heated by gas.

M. J. S.

Detection of Chloral Hydrate in Urine. By VICTOR KULISCH (*Chem. Centr.*, 1897, ii, 391—392; from *Pharm. Post*, 30, 303).—The urine passed in 24 hours is evaporated to a small bulk, acidified with dilute sulphuric acid, and agitated three times in succession with 100 c.c. of a mixture composed of 2 parts of ether and 1 part of alcohol; the ether is then evaporated and the residue distilled with 100 c.c. of hydrochloric acid, sp. gr. = 1.06, or of sulphuric acid, sp. gr. = 1.1. The products of decomposition of any chloral administered and passed into the urine then yield furfuraldehyde, which is readily detected by a test paper impregnated with a solution of xylydine, or aniline, in (50 per cent.) acetic acid. An estimation may be attempted by converting it into furfamide.

L. DE K.

Detection of Acetone in Urine. By A. MALLAT (*J. Pharm.*, 1897, [vi], 6, 296—298).—The author finds that urines which do not give the iodoform test for acetone previously described (*Ann. Méd.*

Thermale, 1886), give the reaction when they have been distilled. It is therefore recommended to always distil over one-fourth of the sample of urine and to test the distillate, after the removal of alcohol, if this is present, by the iodoform test. J. J. S.

Volumetric Estimation of Acetone in Urine. By M. MARTZ (*Chem. Centr.*, 1897, ii, 232—233; from *Rép de Pharm.*, 1897, 197).—Fifty c.c. of the urine is mixed with 1 c.c. of phosphoric acid and distilled until 20 c.c. has passed over; 5 c.c. of the distillate is then mixed in a 250 c.c. flask with 30 c.c. of soda solution and 25 c.c. of iodine solution, and allowed to remain for 25 minutes; a blank experiment is started at the same time, using water instead of urine. Both the liquids are now acidified with 30 c.c. of dilute sulphuric acid (1 : 10), and titrated with N/10 solution of sodium thiosulphate, using 5 c.c. of a 2 per cent. starch solution as indicator. The difference between the two titrations multiplied by 0.001214 represents the amount of acetone.

The iodine solution is prepared by dissolving 25 grams of iodine and 50 grams of potassium iodide and making up to 1 litre; the soda contains 80 grams of sodium hydroxide per litre. L. DE K.

Application of the Carboxime Method for Estimating Carvone in Adulterated Oil of Spearmint. By EDWARD KREMERS and OSWALD SCHREINER (*Chem. Centr.*, 1897, ii, 146; from *Pharm. Rev.*, 1896).—A sample of oil of spearmint adulterated with 33.33 per cent. of cedar-wood oil and 16.66 per cent. of gurgun balsam would still fulfil the requirements of the American pharmacopœia as regards density and polarisation. The percentage of carvone, which in pure oil of spearmint should amount to 56.4 per cent., is, however, reduced to 28.2 per cent. To estimate this carvone, 10 grams of the sample is treated with hydroxylamine, the volatile compounds are driven off in a current of steam, and the residual carboxime is collected, dried, and weighed. L. DE K.

[**Hopkins' Method of Estimating Uric Acid.**] By GOTTFRIED VON RITTER (*Zeit. physiol. Chem.*, 1898, 24, 410—411).—A reply to some strictures passed on the author's work by Folin (this vol., ii, 196). W. D. H.

Estimation of Fat in Milk and Milk Products. By ARTHUR DEVARDA (*Chem. Centr.*, 1897, ii, 151; from *Österr. ung. Zeit. Zucker-Ind. u. Land.*, 1897).—The author recommends the processes devised by Soxhlet and Gerber; the refractometric process of Wollny has not yet been sufficiently tried. To preserve milk for analytical purposes the addition of potassium dichromate or formaldehyde is recommended. L. DE K.

Characteristic Reaction of Cotton-Seed Oil. By GEORGES HALPHEN (*J. Pharm.*, 1897, [vi], 6, 390—392).—Equal volumes (about 1—3 c.c. of each) of the oil under examination, of amyl alcohol, and of carbon bisulphide containing 1 per cent. of free sulphur, are placed in a tube, and the whole then heated in a boiling solution of sodium chloride for 10—15 minutes. If cotton-seed oil is present, a red or

orange coloration is developed; if no coloration is formed, another c.c. of the carbon bisulphide solution is added, and the mixture again warmed.
J. J. S.

Detection of Tallow in Lard. By MATHIAS BALLÓ (*Chem. Centr.*, 1897, ii, 392; from *Zeit. Nahr. Hyg., &c.*, 11, 193—197).—About 60 grams of the melted fat is introduced into the 150 c.c. pear-shaped bulb of a specially-constructed apparatus, and after being allowed to cool for an hour and a half, is placed in ice for another hour. Pure lard absorbs no air, but when even small quantities of tallow are present, a considerable amount of air is absorbed, pure tallow taking up as much as 6·5—8·8 c.c. of air per 100 grams. On dissolving the fat in 100 c.c. of chloroform, the air is liberated, and may be collected in the special burette. It has not yet been determined as to whether the method can be made quantitative.
L. DE K.

Detection of "Saccharin" in Wines. By GIULIO MORPURGO (*Chem. Centr.*, 1897, ii, 531; from *Giorn. di Farm. di Trieste*, 1896, 1, 357).—The "saccharin" now occurring in commerce is not identical with the product sold some years ago, and does not give its reactions. To detect its presence in wine, 400 c.c. of the sample, after being mixed with talc and clean sand, is dried on the water bath, and the powdered residue extracted with 100 c.c. of a mixture of ether and light petroleum, 3 c.c. of phosphoric acid being added. The residue left on evaporating the ether is cautiously dissolved in aqueous soda, and the "saccharin" is then detected by its taste.
L. DE K.

Estimation of Xanthine Bases in Urine. By ROBERT FLATOW and ALBERT REITZENSTEIN (*Chem. Centr.*, 1897, ii, 145—146; from *Deutsch. Med. Wochschr.*, 23, 354—357).—The authors state that if Salkowski's silver process gives correct results, the Krüger-Wulff copper method must be rejected, as this gives about seven times more xanthine bases than the other.
L. DE K.

Separation of Strychnine from Brucine. By G. SANDOR (*Zeit. anal. Chem.*, 1898, 37, 132; from *Apoth.-Zeit.*, 1897, No. 2).—The mixture of alkaloids (0·2 gram) is warmed with just enough 10 per cent. sulphuric acid to dissolve it, and, after cooling, is treated with a solution of 2 grams of potassium permanganate in 100 c.c. of 10 per cent. sulphuric acid until just coloured; the brucine alone is thereby destroyed. The liquid is then made alkaline with ammonia, and shaken with a mixture of 20 grams of chloroform and 30 grams of ether; the filtered chloroform-ether solution leaves the strychnine on evaporation.
M. J. S.

Estimation of Caffeine in Coffee. By ARTHUR FORSTER and RUDOLF RIECHELMANN (*Chem. Centr.*, 1897, ii, 436; from *Zeit. öffentl. Chem.*, 3, 235—236).—A reply to Juckenack and Hilger. When extracting an aqueous solution of caffeine with chloroform, there is no real need for adding aqueous soda, but the authors find that the chloroform layer separates more readily in the presence of soda; the latter has no decomposing action on caffeine.
L. DE K.

Estimation of Urea by means of Formaldehyde. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, 21, 586).—Thoms having tried the author's process of estimating urea by means of formaldehyde in an acid solution, concludes that it is impracticable. His analysis points to the condensation product being methyleneurea.

The author states that, on repeating his analysis, he has obtained the same results as before, and that Thoms' result is untrustworthy.

L. DE K.

Estimation of Tannin by means of Hide Powder. By JOHN H. YOCUM (*J. Soc. Chem. Ind.*, 1897, 16, 419—420).—To secure results which are both uniform and in accord with the practical application of the materials to the production of leather, the following precautions are desirable. The hide should be freed from readily soluble substances by washing immediately before adding it to the tannin solution, a correction being made for the dilution caused by the adhering water. A mechanical means of shaking completes the tanning operation before there is time for the production of more soluble hide. The empirical method of filtration gives comparable results for the soluble solids and the adoption of 20° as the temperature for filtration removes a source of error. The filtrate must be tested for tannin and soluble hide; for the latter, a solution of tannin is a delicate reagent, whilst for the former, a solution of gelatin in dilute alcohol is more sensitive than an aqueous solution. To prepare this, 5 grams of gelatin is dissolved in 100 c.c. of warm water, 40 c.c. of 90 per cent. alcohol is added, and the precipitate is filtered at a temperature a few degrees below that of the atmosphere. It is of great importance that uniform quantities of hide, and solutions of uniform density should be employed in the estimations. The most serious cause of discordance is that different preparations of hide powder do not give the same result.

M. J. S.

Formation of Hæmatin Crystals. By CASIMIR STRYZYOWSKI, *Chem. Centr.*, 1897, i, 295—296; from *Pharm. Post.*, 30, 2—4).—In the production of Teichmann's hæmin crystals, sodium chloride may be replaced by sodium bromide or iodide. The hydrobromide and the hydriodide crystals have the same form as the hydrochloride but are darker coloured, being nut-brown and brownish-black respectively. As it seemed possible that the sodium chloride present in the blood might have taken part in the production of the crystals, the experiments were repeated with pure hæmatin; the same results were obtained.

The employment of sodium iodide is recommended for forensic purposes, as, owing to the darker colour of the crystals, as little as 0.000025 gram of fresh blood can be detected.

N. H. J. M.

General and Physical Chemistry.

Atomic Refraction of Fluorine. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1897, ii, 1042—1043; from *Bull. Acad. roy. Belgique*, 1897, [iii], 34, 293—307).—Using the Lorenz formula and Conrady's values for the atomic refractions of carbon, hydrogen, and oxygen, the author has calculated the atomic refractions of fluorine, chlorine, and bromine in saturated and unsaturated compounds. The values obtained were, for chlorine, 5·9028 in saturated, and 6·001 in unsaturated compounds; for bromine, 8·762 in saturated, and 8·759 in unsaturated compounds; for fluorine, 1·082 in saturated, and 0·775 in unsaturated compounds. The difference between the two values is therefore far more pronounced with fluorine than with either chlorine or bromine. A possible explanation of this is, that fluorine in unsaturated compounds behaves as a polyvalent element, and that in those compounds the carbon atoms are no longer doubly linked. If this is the case, the true atomic refraction of fluorine in these compounds is 0·775 *plus* the value for the double linking, 1·707, and therefore 2·482. The atomic refraction of fluorine in saturated compounds is about equal to that of hydrogen, 1·051. If the double linking is present in the unsaturated fluorine compounds, in these fluorine has the smallest atomic refraction of any known element. This is in keeping with the fact that fluorine has also the smallest atomic volume.

H. C.

Rotatory Power of Polymerised Compounds. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, 125, 822).—In connection with the researches of Guye and Aston, the author calls attention to his early researches on the rotatory power of isoterebenthene ($[\alpha]_D = -10\cdot0^\circ$) and metaterebenthene ($[\alpha]_D = -3\cdot3^\circ$) (*Ann. Chim. Phys.*, 1853, [iii], 39, 16), and styrene ($[\alpha]_D = -3\cdot4^\circ$) and metastyrene ($[\alpha]_D = -2\cdot2^\circ$) (*Abstr.*, 1878, 296).

C. H. B.

Flame Spectrum of Carbonic Oxide. By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1897, 61, 217—219).—In the flame spectrum of carbonic oxide previously examined by the author (*Phil. Trans.*, 1895, 185, A, 176), faint lines were observed, coincident with the edges of carbon bands present in the flame of coal gas. Since these might have been due to carbonaceous dust, or to traces of volatile hydrocarbons, the spectrum obtained under conditions which exclude the presence of such impurities has been examined, using a narrower slit than formerly, to ensure better definition. Whilst no carbon bands or lines were photographed, two groups of lines of the water-vapour spectrum (Liveing and Dewar, *Phil. Trans.*, 179, 27) were observed, which were identified by comparing them with those obtained from the flame of an oxy-hydrogen blow-pipe. The same lines were also visible when both the oxygen and carbonic oxide had been carefully dried, although not present in the original photograph of the carbonic oxide spectrum (*loc. cit.*). In the latter case, their invisibility was probably due to the lack of definition caused by the wider slit. The lines probably owe

their origin to the moisture of the atmosphere; their presence is, possibly, a confirmation of Dixon's observation (*Trans.*, 1886, 94), that dry carbonic oxide will not burn in dry air, although Smithells (*Trans.*, 1894, 610) states that it will burn if previously heated.

Since the relative intensities of the two groups of lines are not the same as in Liveing and Dewar's photographs, it is possible that they belong to the spectra of two different substances, one of which is possibly an oxide of nitrogen. W. A. D.

Spectrochemistry of Nitrogen. VI. Oxygen Compounds of Nitrogen. By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1898, 25, 577—650).—The spectrometric constants of the group $\cdot\text{NO}_3$ do not differ to any appreciable extent in the alkylic nitrates and nitric acid, whilst, further, the values for NO_2 , obtained by comparison of the nitrates with the alcohols also agree, so that the constitution of these compounds must be regarded as similar to that of nitric acid. The value of the NO_2 -group further agrees with that of the same group in the alkylic nitrites, but is considerably greater than in the nitro-compounds. Concordant values for the N_2O_2 -group are obtained from the primary and secondary nitramines and the substituted nitro-urethanes, so that the author concludes that even if the group N_2O_2 is not identical in structure in the three classes of compounds, yet there can be no saturation difference, and similar results also hold for the NO_2 -group. The nitroso-compounds are next examined, and the spectrometric constants for the NO and N_2O -groups determined for a number of nitrosamines; the values obtained agree well among themselves, but the results for NO do not agree with those obtained from the nitrites, probably owing to the influence of the oxygen in the latter compounds. In the hydrazines, although the values for N_2 differ considerably, yet those of the primary nitrogen alone agree well in all the compounds, being equal to the constants obtained for the nitrogen of hydroxylamine and ammonia. The refraction of the N_2 group in the diazo-compounds is 8.41, or about 3.4 higher than that of the same group in the primary hydrazines, whilst the refraction for N_3 in diazobenzeneimide is 10.37, that is, again 3.4 higher than that of three hydrazine nitrogens, so that the diazo-nitrogens have an undoubtedly higher value than those of hydrazine, the difference being considerably greater than that due to an ethylenic linking. The author then considers the bearing of these results on the question of the constitution of the various compounds. In azoxybenzene, the value for the N_2O -group is 11.9, whilst that calculated on the assumption of a single linking between the nitrogen atoms is 7.5, so that azoxybenzene must be regarded as a compound of the diazo-structure with the formula $\text{O} \begin{smallmatrix} \diagup \text{N} \text{Ph} \\ \diagdown \text{N} \text{Ph} \end{smallmatrix}$ or $\text{Ph} \cdot \text{N} \begin{smallmatrix} \diagup \text{N} \cdot \text{Ph} \\ \diagdown \text{O} \end{smallmatrix}$. For similar reasons, the author considers that nitrosoethylurethane and its homologues are analogous in structure to the diazo-compounds, the formula $\begin{smallmatrix} \text{N} \\ \diagup \text{O} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{R} \\ \diagdown \text{CO} \cdot \text{R} \end{smallmatrix}$ being suggested. The constants obtained for nitrous oxide and free nitrogen do not lead, however, to any definite structural formulæ. The constitution of the nitramines is discussed at considerable length,

various suggested formulæ are considered, that which is best in accord with the chemical and physical properties being $\begin{matrix} x \\ y \end{matrix} > \text{N} \begin{matrix} \diagup \diagdown \\ \diagdown \diagup \end{matrix} \text{N}$. The

comparison of the nitrites with the nitro-paraffins leads to the formulæ $\text{RO}\cdot\text{N}\cdot\text{O}$ and $\text{R}\cdot\text{N} \begin{matrix} \diagup \diagdown \\ \diagdown \diagup \end{matrix} \text{O}$ for these classes of compounds, the metallic

nitrite possessing a constitution similar to that of the alkylic compounds. The formation of a nitro-paraffin from silver nitrite is hence explained, thus: $\text{AgO}\cdot\text{N}\cdot\text{O} + \text{MeI} = \text{AgO}\cdot\text{NMe}\cdot\text{O}\cdot\text{I} = \text{AgI} + \text{Me}\cdot\text{N} \begin{matrix} \diagup \diagdown \\ \diagdown \diagup \end{matrix} \text{O}$. As the re-

fraction of the NO_2 -group in the nitric acid and the nitrates differs from that in nitro-compounds, the group $\cdot\text{N} \begin{matrix} \diagup \diagdown \\ \diagdown \diagup \end{matrix} \text{O}$ is absent in the

nitrates, and as the complex $\text{O}=\text{N}=\text{O}$ should, on account of the two doubly-linked oxygens and a quinquivalent nitrogen, possess a much higher value than that actually found, the author concludes that this group is also absent, and that the formula best in accord with the spectrometric values is $\cdot\text{O}\cdot\text{O}\cdot\text{N}\cdot\text{O}$, and the formation of nitro-compounds from nitric acid is explained on this assumption. The author further suggests that in nitric acid itself the union of the atoms is not rigid, so that the hydrogen is united with different oxygens in turn (*Abstr.*, 1897, ii, 297).

L. M. J.

Electromotive Behaviour of Chromium. By WILHELM HITTORF (*Zeit. physikal. Chem.*, 1898, 25, 729—749).—In dilute halogen acids or sulphuric acid, chromium dissolves on the application of heat with the formation of chromous compounds; nitric, chloric, chromic, phosphoric, citric, tartaric, formic, and acetic acids; caustic potash and caustic soda have, however, no action either hot or cold. In its electrical properties it was found to be electronegative, not only to zinc, but also to cadmium, iron, nickel, copper, mercury, and silver, and is inactive in salt solutions of these metals except in that it reduces mercuric or cupric to mercurous or cuprous salts. When employed as anode in solutions in which it is indifferent, it was found to become covered with a yellow film of chromic acid, and the loss of weight of the anode was found to correspond with the production of sexavalent chromium ions; this occurs even in solutions of hydrogen chloride in which chromium ordinarily dissolves with the formation of chromous salts. This may be due either to the decomposition of the water by the anion and subsequent formation of chromic acid from the liberated oxygen, or to the formation of a compound of sexavalent chromium with the anion and the decomposition of this compound by water; no such compound, however, is actually known to exist. In solutions of potassium thiocyanate or of an iodide, the chromium anode experiences no loss. A chain of the type, $\text{Cr} \mid \text{KCl} \mid \text{NaNO}_3 \mid \text{AgNO}_3 \mid \text{Ag}$, gave no electromotive force at 5° , and the same result obtained when a dilute acid was used in place of the potassium chloride solution; when measured against 2 Daniells cells, an E.M.F. of 0.4D was obtained. When the acid employed, however, was sufficiently strong

to cause dissolution of the chromium and evolution of hydrogen, an E.M.F. of 1.056 volts was found. When the metal was used for the electrolysis of melted potassium chloride or zinc chloride, totally different results were obtained, and the loss of weight of the anode proved that bivalent chromium ions were produced, and similar results were also found in solutions at 100°, of the halogen acids, of potassium chloride, cyanide, bromide, or iodide, of barium chloride or ammonium chloride, and in solutions of zinc or magnesium chloride at higher temperatures. In solutions of the salts of easily reducible metals, such as cadmium or copper, the chromium was still found to produce sexavalent ions. Corresponding with this change in the activity of the chromium, a change was also found in E.M.F. of the cell previously examined, the value of 1.05 volts being reached at 100°, when such a cell forms a constant galvanic element. In melted oxygen salts or in oxygen acids at 100°, sexavalent ions were still found to exist, so that the E.M.F. of a cell of the type $\text{Cr} \mid \text{SO}_4\text{K}_2 \mid \text{NaNO}_3 \mid \text{NO}_3\text{Ag} \mid \text{Ag}$ remains practically constant when raised to 100°. By the use of alcoholic solutions of zinc chloride, the trivalent ions were also obtained. The inactivity of the chromium is compared with the passive state of iron, but the author considers that the explanation assigned to the latter phenomenon, namely, the formation of a film of oxide, cannot apply to the former case.

L. M. J.

Electromotive Behaviour of Cadmium Amalgams of Different Composition. By WILHELM JAEGER (*Ann. Phys. Chem.*, 1898, [ii], 64, 106—110).—As cadmium cells are employed in place of zinc cells as standards in E.M.F. measurements, it is of importance to ascertain in how far their behaviour depends on the composition of the cadmium amalgam they contain. Direct measurements show that amalgams containing from 5 to 15 per cent. of cadmium exercise the same influence on the E.M.F., as this is not found to vary within one-hundredth of a millivolt. Amalgams containing more than 15 per cent. of cadmium do not give constant results, the E.M.F. rising gradually to that given by cadmium alone. An amalgamated cadmium rod is at first found to give the value obtained for the weak amalgams, but in a short time the E.M.F. rises in the direction of that of pure cadmium. This is evidently due to the diffusion of the mercury into the cadmium.

H. C.

Electrolysis of Hydrochloric Acid and Cathodic Formation of Lead. By FRITZ HABER (*Zeit. anorg. Chem.*, 1898, 16, 438—449).—Electrolysis of hydrochloric acid with platinum or platinum-iridium electrodes is found to result in an attack of the platinum at ordinary temperature when the acid is concentrated, but the platinum remains unaffected when the concentration is below 30 per cent. HCl. Platiniridium containing 10 per cent. of iridium is hardly attacked at all by the concentrated acid, and if the alloy contains 20 per cent. of iridium it remains unaffected. At the boiling point, an 11 per cent. acid solution attacks the platinum as vigorously as a 36 per cent. solution at the ordinary temperature, but an 8 per cent. solution leaves the platinum intact. During the course of the electrolysis, a deposition of platinum on the cathode is observed, but this is not due to transference

of platinum from the anode to the cathode, as the cathode loses in weight. It is probably due to mechanical action and in some way connected with the absorption of gases by the platinum. Lead is found to behave in a similar manner, so that formation of a layer of spongy lead on the cathode can be obtained by the electrolysis of sulphuric acid with lead electrodes.

H. C.

Electrolysis of Hydrochloric Acid. II. By FRITZ HABER and S. GRINBERG (*Zeit. anorg. Chem.*, 1898, **16**, 329—361. Compare this vol., ii, 215).—In continuing their investigation of the electrolysis of hydrochloric acid, the authors have made experiments with acid to which either sodium hydroxide or magnesia had been added in sufficient quantity to effect a neutralisation of two-thirds of the acid; they have also carried out investigations with the pure dilute acid at 100°. The presence of sodium hydroxide or magnesia has little effect on the evolution of oxygen from the dilute acid. Heating the acid brings about a most marked increase in the evolution of oxygen, which was found in one case to constitute 88.2 per cent. of the gas from the anode. The amount of chloric acid formed is, however, decreased to mere traces, unless the acid is largely diluted with water. Perchloric acid is also found in very small quantity. A full theoretical discussion is given by one of the authors. (F. H.).

H. C.

Migration Constants of Zinc and Cadmium Salts in very Dilute Solutions. By GOTTFRIED KÜMMELL (*Ann. Phys. Chem.*, 1898, [ii], **64**, 655—679).—The author finds that limiting values for the migration constants of zinc and cadmium salts can be directly determined with the haloid compounds when the dilution is $\frac{1}{100}$ to $\frac{1}{500}$ normal, and that these values are in keeping with the Kohlrausch law. The sulphates, however, appear to contain complex ions of the character $S_4O_6ZnSO_4$, and therefore do not give results consistent with the Kohlrausch law in these dilutions. Combining his results with the conductivity determinations of Wershofen and Kohlrausch, the author gives the following apparent rates of transference U and V for the positive and negative ions respectively, the concentrations, c , being given in equivalents per litre.

c.	$\frac{1}{2}CdCl_2$			$\frac{1}{2}CdBr_2$			$\frac{1}{2}CdI_2$			$\frac{1}{2}ZnCl_2$		
	$\lambda \cdot 10^7$	$U \cdot 10^7$	$V \cdot 10^7$	$\lambda \cdot 10^7$	$U \cdot 10^7$	$V \cdot 10^7$	$\lambda \cdot 10^7$	$U \cdot 10^7$	$V \cdot 10^7$	$\lambda \cdot 10^7$	$U \cdot 10^7$	$V \cdot 10^7$
0.002	94	39	54	92	39	53	86	39	47	98	39	59
0.005	85	36	49	80	34	46	72	32	40	—	—	—
0.006	—	—	—	—	—	—	—	—	—	94	38	55
0.01	77	32	45	71	30	41	61	27	33	91	37	54

H. C.

Electrostenolysis. By ALFRED COEHN (*Zeit. physikal. Chem.*, 1898, **25**, 651—656).—From the law that when two dielectrics are in contact, that with the higher dielectric constant becomes positive to the other, it follows that water, owing to its very high constant, becomes

positive to the walls of the containing vessel, and hence the metallic ions form a layer on the wall and the acid ions the corresponding film of the 'double layer.' The quantity of metal so precipitated is too small to be visible, but in the case of a layer so formed in a crack in the partition separating two similar solutions containing electrodes, the quantity may be increased if the addition at the cathodic end exceeds that dissolved at the anodic end, in which case Braun's "electrostenolysis" (Abstr., 1891, 393) will occur. This happens : (1) when the negative radicle does not act on the precipitated metal ; (2) when insoluble compounds, usually peroxides, form at the anode ; (3) when the negative ion reacts with the solution to form salts of a higher oxide ; and the author points out that all the cases of electrostenolysis observed by Braun are due to one or other of these causes.

L. M. J.

Determination of the Conductivity of Liquids in Thin Layers. By G. B. BRYAN (*Phil. Mag.*, 1898, [v], 45, 253—272).—According to Koller (*Wien. Ber.*, 1889, 98, iia, 201), the specific conductivity of certain liquids decreases as the thickness decreases. By careful repetition of Koller's experiments with new and improved apparatus, the author has been able to prove that for dilute solutions, alcohol and aniline, the conductivity is the same for all thicknesses within the limits of the experiments. It has been found that the great differences obtained by Koller for water and alcohol can be eliminated by taking care that the plates are true and clean, and by using an alternate current instead of a continuous one.

H. C.

Calculation of the Conductivity of Aqueous Solutions Containing Two Electrolytes with no Common Ion. By JAMES G. MACGREGOR and E. H. ARCHIBALD (*Phil. Mag.*, 1898, [v], 45, 151—157).—According to the dissociation theory, the specific conductivity of a complex solution, volume v of which contains N_1 , N_2 , N_3 , &c., gram equivalents of the electrolytes 1, 2, 3, &c., respectively, is given by the expression, $\frac{1}{v}(a_1N_1\mu_{\infty 1} + a_2N_2\mu_{\infty 2} + a_3N_3\mu_{\infty 3} + \&c.)$,

where the a 's are the coefficients of ionisation of the electrolytes and the μ_{∞} 's their specific conductivities per gram equivalent at infinite dilution. It is shown how equations sufficient for the determination of the a 's and N 's may be obtained for solutions containing two electrolytes with no common ion. A series of observations and calculations of the conductivity of solutions containing sodium and potassium chlorides and sulphates was made to test the results. The agreement between the observed and calculated values in the case of the more dilute solutions is satisfactory.

H. C.

New Basis for the Values of the Conductivities of Electrolytes. By FRIEDRICH KOHLRAUSCH, L. HOLBORN, and H. DIESSELHORST (*Ann. Phys. Chem.*, 1898, [ii], 64, 417—455).—The object of this investigation was to obtain accurate determinations of the conductivities of a number of normal electrolytes, and to employ these values for the purpose of revising the older data with reference to conductivities, as well as to furnish numbers that might be used as standards in future determinations. The unit of conductivity selected is that of a substance of which 1 centimetre cubed has a resistance of 1 ohm. This

conductivity is denoted by κ , and the conductivity in electromagnetic units is therefore $\kappa \cdot 10^9$. Solutions of strong monobasic acids, which have the greatest conductivity, would approximate to the above unit conductivity at 38—40°. At the ordinary temperature, accumulator sulphuric acid has a value of about 0.7; concentrated copper sulphate, 0.05; concentrated sodium chloride, 0.2; and good distilled water 10^{-6} . For mercury at 0°, $\kappa = 10630$.

The following values were obtained for the standard electrolytes examined.

Sulphuric acid, of maximum conductivity, density $18^\circ/4^\circ = 1.223$, containing about 30 per cent. H_2SO_4 , $\kappa_{18} = 0.7398$.

Magnesiumsulphate, of maximum conductivity, density $18^\circ/4^\circ = 1.190$, about 35.6 per cent. MgSO_4 , $\kappa_{18} = 0.04923$.

Sodium chloride, saturated solution, $\kappa_{18} = 0.21605$.

Potassium chloride, normal solution, $\kappa_{18} = 0.09822$.

" " $\frac{1}{10}$ " " $\kappa_{18} = 0.01119$.

" " $\frac{1}{50}$ " " $\kappa_{18} = 0.002397$.

" " $\frac{1}{100}$ " " $\kappa_{18} = 0.001225$.

Experiments were made at temperatures between 0° and 36°, in order to determine accurately the influence of temperature on the conductivities of the above solutions. The results are given in tabular form.

To convert values obtained in the older determinations, and expressed in mercury units k into the units now employed, they should theoretically be multiplied by the factor 10630. But as several sources of error, as, for example, in the temperature measurements, are known to exist, it would appear that the value of the factor for the determinations of Kohlrausch and Grotian, Kohlrausch, Loeb, and Nernst, MacGregory, and Sheldon is about 10691. For determinations made in Ostwald's laboratory, the factor 10660 may be taken. H. C.

Determination of the Boiling Point of Aqueous Solutions with Beckmann's Apparatus. By WILHELM MARCKWALD and A. CHWOLLES (*Ber.*, 1898, 31, 791—795).—More concordant results were obtained than are commonly supposed to be attainable; the following precautions were observed. (1) Two apparatus were used. Water was first boiled in both, and the difference between the readings of the two thermometers was noted. The water in one was then replaced by the solution to be examined, and the difference between the two thermometers again noted. By subtracting the first difference from (or adding it to) the second, the raising of boiling point in the solution is obtained, free from any error that variation of the atmospheric pressure might otherwise have introduced. (2) For a month before use both thermometers were heated each day to 120—160° in glycerol and allowed to cool slowly during the night; this treatment was necessary in order to secure a constant difference between the two thermometers when both were immersed in boiling water. In each separate series of determinations, the difference between the readings of the two thermometers varied at most by $\pm 0.004^\circ$ to 0.006° , whilst the raising of the boiling point varied in the different series from 0.065° to 0.165° ; the solutions experimented with were those of cinchonine hydrogen *d*-tartrate and *l*-tartrate.

The boiling vessel is best made of Jena glass with a thin platinum

wire fused into the bottom; those of Thuringian glass, with a thick wire, crack very soon. The apparatus is heated very cautiously with a ring-burner slightly larger in diameter than the porcelain mantle, and finally a long, thin, smoky flame is lighted under the boiling vessel; $1\frac{1}{4}$ — $1\frac{1}{2}$ hours elapses before the temperature becomes constant. C. F. B.

Heat of Separation in Solutions: Freezing Point Reduction: Solubility. By ALBERT DAHMS (*Ann. Phys. Chem.*, 1898, [ii], 64, 507—518).—By "heat of separation," the author denotes all heat changes which accompany the removal of one of the constituents from a solution, as heat of vaporisation or solidification of the solvent. Thermodynamical considerations lead to the general law of solubility enunciated by Schröder (Abstr., 1893, ii, 366), and Le Chatelier (Abstr., 1894, ii, 272). A satisfactory agreement with the theory is obtained for solutions of ethylenic bromide in naphthalene, ethylenic bromide and benzene in diphenylamine, and diphenylamine in ethylenic bromide. Exceptions are observed in other cases, and these the author refers in the first place to the influence of temperature on the latent heat of fusion. If the latent heat of fusion, r , changes with temperature, so that $r = r_0 + a(t_0 - t)$, the Schröder-Le Chatelier formula then becomes

$$\log s = \frac{r_0 + \frac{a}{2}(t_0 - t)}{R} \left(\frac{1}{t} - \frac{1}{t_0} \right) \quad \text{H. C.}$$

Determinations of the Freezing Point Reductions of Dilute Solutions and their Relation to the Theories of Solutions. By RICHARD ABEGG (*Ann. Phys. Chem.*, 1898, [ii], 64, 486—506).—A critical examination of the determinations of the freezing point reductions of dilute aqueous solutions which have been made by Raoult, Jones, Loomis, Nernst and Abegg, Wildermann, and Ponsot, leads the author to conclude that the more trustworthy the method adopted and the results obtained, the closer the agreement between these results and those required by the theories of Van't Hoff and Arrhenius. The vapour pressure determinations of Dieterici (*Ann. Phys. Chem.*, 1897, [ii], 62, 616), are also criticised, and the want of agreement between the results obtained and those required by the above theories is shown to be probably due to experimental error. H. C.

Thermochemistry of Hydrobenzamide Amarine, and Lophine. By MARCEL DELÉPINE (*Compt. rend.*, 1897, 125, 178—181).—Amarine crystallises with $\frac{1}{2}$ H₂O, and in this hydrated form melts at 100°; when anhydrous, it melts at 129°.

	Heat of combustion		Heat of formation.	Heat of solution and of neutralisation.
	(1) At constant volume.	(2) At constant pressure.		
Hydrobenzamide	2666·1 cal.	2668·1 cal.	— 66·8 Cal.	
Hydrated amarine.....	2651·2	2653·2	— 51·9	4·8 Cal.
Anhydrous „	2651·4	2653·4	— 52·1	6·1
Lophine	2585·85	2587·6	— 55·3	

$3\text{C}_6\text{H}_5\text{CHO}$ liq. + 2NH_3 diss. = $(\text{C}_6\text{H}_5\text{CH})_3\text{N}_2$ sol. + $3\text{H}_2\text{O}$ (liq.) + 2×11 Cal.

$\text{C}_{21}\text{H}_{18}\text{N}_2$ (amarine) sol. + $\text{O} = \text{C}_{21}\text{H}_{16}\text{N}_2$ sol. + H_2O liq. + 66.6 Cal.
J. J. S.

Determination of the Molecular Weight of Solid Substances. By ISIDOR TRAUBE (*Ber.*, 1898, 31, 1081—1083. Compare this vol., ii, 213).—The author, in reply to the criticism of Fock (this vol. ii, 284), maintains the accuracy of his previous deduction that most solid compounds have twice the molecular weight usually ascribed to them. He also points out that Fock is not justified in applying the equation $c \frac{(1-\gamma)}{x} + \frac{c\gamma}{\sqrt{x}} = \text{const.}$ to strong electrolytes, in the way in which he has employed it in his method for determining the molecular weights of solid substances (*Abstr.*, 1897, ii, 481; this vol., ii, 154).
A. H.

Supersaturation and its Dependence on Crystalline Form. By WILLIAM W. J. NICOL (*Zeit. anorg. Chem.*, 1897, 15, 397—404).—The author advances the view that when, under the conditions of the experiment, two allotropic modifications of the dissolved or molten substances are capable of existing, the occurrence of supersaturation or superfusion becomes possible. By allotropic is here understood not merely amorphous and different crystalline forms of the same substance, but such different crystalline modifications as may owe their existence to the presence or absence of water of crystallisation, or other foreign molecules. Thus a supersaturated solution of sodium thiosulphate deposits, on evaporation at ordinary temperature, not only crystals containing $5\text{H}_2\text{O}$, but also crystals which probably contain $2\text{H}_2\text{O}$. Sodium sulphate, as is well known, gives both the decahydrate and a heptahydrate. Borax can be obtained either as decahydrate or pentahydrate, and similar allotropic forms were observed with barium chloride and lead acetate. The deposition of different allotropic crystalline forms from supersaturated solutions was observed with the nitrates of potassium, ammonium, and silver, and among organic compounds with acetanilide, quinol, acetamide, resorcinol, and malonic, mandelic, tartaric, and citric acids.

H. C.

Crystallisation of Overcooled Benzophenone. By KARL SCHAUM (*Zeit. physikal. Chem.*, 1898, 25, 722—728).—The author had previously observed that benzophenone contained in various tubes which had been heated for some time above its melting point, solidified at different temperatures, although the tubes were all treated alike, and, therefore, considered it probable that the nature of the surface in contact with an overcooled liquid affects the temperature of solidification. To test this, 62 tubes of benzophenone were prepared, and in about 30 were placed small pieces of glass, pumice, or marble, garnets, sand, &c., whilst the interior of some of the tubes was previously etched by hydrogen fluoride or coated with fat. The tubes were then kept at 52° for 30 minutes and allowed to cool,

the temperature being noted at which solidification occurred in each tube. The effect of the added substance is, in general, to increase the tendency to solidify, the sand having the most marked effect. Repeated melting diminishes this tendency, as in the first series of experiments 40 tubes, and in the sixth series only 10 tubes, solidified at the temperature of the air. Long heating and very gradual cooling favour the overcooling, and at low temperatures produced by carbonic anhydride and ether the benzophenone solidifies to a glassy mass. In all the experiments, the stable modification of the compound was alone obtained.

L. M. J.

The Equilibrium, $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, and the Study of Explosives. By C. HOITSEMA (*Zeit. physikal. Chem.*, 1898, 25, 686—698).—In most cases of the combustion of explosives in insufficient oxygen, the chief products of the reaction are carbonic anhydride, carbonic oxide, water, and free hydrogen, so that at the temperature of the explosion these gases are in equilibrium, and from the quantities of the several components, the equilibrium constant may be calculated for the reversible reaction, $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. At ordinary temperatures, the velocity in either direction is practically zero, but at 600° the direct action, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, becomes measurable, although the reverse action cannot be observed below about 900° (Naumann and Pistor, *Abstr.*, 1886, 16, 120). From the results of Macnab and Ristori's (*Abstr.*, 1895, ii, 434) determinations of the composition of the gaseous products, and of the heat produced by different explosives, the author calculates the temperature of the explosion and the equilibrium constant for the above reaction; this constant is found to increase with temperature from about 4 at 2200° to 5 at 2800° . From Horstmann's researches on the incomplete combustion of mixtures of carbonic oxide and hydrogen, further data are obtained for the determination of the constant, and in each set of experiments a maximum value is indicated at a temperature varying from 2500° to 2900° , the mean being 6.25 at 2670° . This maximum value should occur at the temperature at which the heat development is zero, and by the aid of Mallard's and Le Chatelier's formulæ for the specific heats of the various gases, this temperature is calculated to be 2825° , a number lying between that indicated by the two sets of determinations, which the author considers agree as well as could be expected, many factors, the dissociation of the product, for instance, not being determined.

L. M. J.

The author makes no mention of Dixon's determinations of the equilibrium constant, nor of any of the same author's numerous researches on this subject (*Trans.*, 1886, 94; *Abstr.*, 1885, 479).

L. M. J.

Explanation of the Exceptions observed in the Speed of Chemical Changes in Solution. By ERNST COHEN (*Chem. Centr.*, 1897, ii, 460; from *Maandbl. Natuurw.*, 1897, 21, 47—53).—The rate of inversion of cane-sugar is, according to Ostwald, given by the equation $K = \frac{1}{t} \log \frac{A}{A-x}$, where t is time, A the amount of sugar originally present, and x the amount that has undergone change in the time t .

Exceptions are, however, observed from this, the normal behaviour. Thus, when $A = 40$ per cent., $K = 29.16$, but when $A = 4$ per cent., K is only 19.15 . The exceptions are due to the volume of the sugar being left out of consideration; for if the amount of acid is the same in both cases, the volume in which sugar molecules and acid molecules meet is smaller in the case of a 40 per cent. than with a 20 per cent. sugar solution, and, consequently, the rate of inversion is greater. In this case $K_{40} : K_{20} = 1/(100 - b_{40}) : 1/(100 - b_{20})$, where b_{40} and b_{20} are the volumes occupied by 40 and 20 grams of sugar respectively in the solution. Or, for the general case, $K_p : K_q = C_p/(100 - b_p) : C_q/(100 - b_q)$, where C_p and C_q are the concentrations of the acid. The author has tested these equations experimentally, and finds that they hold.

H. C.

Separation of Racemic Compounds by means of Optically Active Substances. By WILHELM MARCKWALD and A. CHWOLLES (*Ber.*, 1898, 31, 783—790).—There are still adherents to Pasteur's opinion that, if racemic acid can be separated into *r*- and *l*-tartaric acids by crystallisation of its quinine, but not of its potassium, salt; if, that is, "quinine does not behave in the same way with respect to the two tartaric acids as potash does, this is only because it is asymmetrical, whilst potash is not. Asymmetry is thus a property which is in itself capable of altering chemical affinity." Now it is opposed to modern views of affinity that two acids which have an identical constant of affinity with respect to one base, potash, should have different constants with respect to another base, quinine. In fact, the authors find that *r*- and *l*-tartaric acid have an identical constant of affinity in respect to both cinchonine and nicotine, which are both optically active, and, therefore, asymmetrical; for solutions of equivalent strength of the cinchonine hydrogen salts of these two acids exhibit a raising of the boiling point of the water by the same amount; and the methylic salts of the two acids are hydrolysed at the same rate by nicotine, both at 17.5° and at 40° (decinormal aqueous solutions of the two reacting substances were mixed in equal proportions by volume).

The following explanation is adopted. The potassium salts of two optically isomeric acids are, like the acids themselves, images of each other in a mirror; they would, therefore, not be expected to have different solubilities, nor, in consequence, to be separable by crystallisation; but when the two acids form salts with an optically active base, the two compounds formed, each of which now contains two asymmetric systems, are no longer related as object to image, and might, therefore, be expected to exhibit a difference in solubility such as would render it possible to separate them by crystallisation. It is this physical difference between the two salts that determines the possibility of separation, not a difference in the extent of chemical action of the two acids on the base; for, when inactive methylethyl-acetic acid, or inactive mandelic acid, is treated with (optically active) brucine, in amount just sufficient to neutralise half of the acid, *care being taken that enough water is present to keep the brucine salt dissolved*, the acid that can be removed from the solution by extraction

with ether is found to be optically inactive. No separation into optically active constituents has been effected by the purely chemical action of the optically active base; it is only when physical differences come into play, such as the difference of solubility manifested in the one salt crystallising out before the other, that a separation of the constituents is attained.

Incidentally, *normal cinchonine l-tartrate* was prepared; like the *r*-isomeride, it crystallises with $2\text{H}_2\text{O}$, and both substances are partially decomposed by water into cinchonine and the hydrogen tartrate.

C. F. B.

Hylotropically Isomeric Substances. By KARL SCHAUM (*Annalen*, 1898, 300, 205—228).—The term “hylotropic” has been proposed by Ostwald to denote such substances or mixtures of substances as are capable of undergoing change into others in such a manner that the elementary composition of the original substances is the same as that of the products of reaction. Thus, the substances standing on either side of a chemical equation are hylotropic. All compounds which may change directly into isomeric compounds are hylotropically isomeric. These may be divided into two groups: physically isomeric hylotropic substances, in which the isomerism depends on a difference in the energy content, and chemically isomeric hylotropic substances, which owe their difference to differences in the chemical molecules. Physically isomeric substances are always hylotropic, but this is not true of chemical isomerides. Polymorphous substances are physically isomeric, and form the main class of hylotropic substances of this order; in the liquid state, experiments, which the author quotes, with hexachlor- α -keto- β -*R*-pentene show that the physical isomerism which holds for the solid (see Küster, *Abstr.*, 1896, ii, 158) is not maintained. Chemical hylotropism is most frequently due to polymerisation and dissociation. Some special cases are discussed by the author.

H. C.

Condensation of Water Vapour in Presence of Dust-free Air and other Gases. By C. T. R. WILSON (*Proc. Roy. Soc.*, 1897, 61, 240—242).—When air, oxygen, nitrogen, chlorine, or carbonic anhydride, initially saturated with moisture, and free from all foreign nuclei, is allowed to expand suddenly, a rain-like condensation takes place if the expansion exceeds a certain critical limit; on increasing the expansion, a second definite limit is reached, beyond which the condensation is cloud-like, the number of drops formed increasing at a very rapid rate with increasing pressure. In the case of hydrogen, the cloud-like condensation alone takes place.

Values are given for the limits of expansion and supersaturation which correspond with the two forms of condensation; these are apparently the same for all the gases examined except hydrogen, which, however, shows the cloud-like condensation at the same limit as the other gases. The Röntgen rays have the effect of greatly increasing the number of drops during condensation, the minimum expansion required for the latter remaining unaltered.

W. A. D.

Lecture Experiments. By JOHN WADDELL (*Chem. News*, 1898, **77**, 131).—Attention is drawn to the colour changes produced by solvents; alcohol or acetone causes the colourless solution of cyanine in acetic acid to turn blue; the red solution of methyl-orange in acetic acid to become yellow; acetone also changes the red solution of corallin in concentrated ammonia to yellow; all these changes are reversed by the addition of water, but again restored by the further addition of alcohol or acetone. The green colour of an ammoniacal solution of paranitrophenol is rendered lighter by adding concentrated ammonia and acetone, and is discharged by a further addition of ether: alcohol or, more especially, water, restores the green colour. A concentrated solution of phenolphthalein in acetone is scarcely coloured by strong ammonia, but a further addition of water develops the characteristic red colour.
D. A. L.

Laboratory Notes. Asbestos. Combustion Furnaces. By H. JERVIS (*Chem. News*, 1898, **77**, 5—6).—The author draws attention to the facility with which asbestos may be moulded when wet, retaining the form so given to it when dried, these properties can be applied to the preparation of asbestos plugs, tips for burners, and arched and perforated covers for the combustion furnace; the diminished weight in the latter case, as compared with tile covers, permits of a much lighter structure for the furnace itself, and the author proposes the use of a piece of sheet iron suitably shaped for the purpose.
D. A. L.

Inorganic Chemistry.

Hyponitrous Acid. By A. KIRSCHNER (*Zeit. anorg. Chem.*, 1898, 16, 424—437. Compare Divers and Haga, *Trans.*, 1889, 760 ; 1894, 529).—Hyponitrous acid is prepared as follows. Potassium oxyimido-sulphonate (50 grams) is dissolved in boiling water (35 c.c.) and then, after cooling with ice, mixed with concentrated sodium hydroxide (1 : 1, 10 c.c.), care being taken that the temperature does not exceed 30°. The mixture is cooled to 10°, and 90 c.c. more of the sodium hydroxide added, the mixture heated at 50° for $\frac{1}{2}$ to $\frac{3}{4}$ hour and then poured into a litre of water. The resulting solution contains sulphate, sulphite, and hyponitrite, together with small quantities of undecomposed oxyamido-salt and hydroxylamine. The last two compounds are destroyed by the addition of yellow mercury oxide and the clear filtered solution made up to 4 litres and precipitated with silver nitrate as long as a light yellow precipitate of silver hyponitrite is obtained. The precipitate is finally washed with warm water until the wash water is neutral.

Barium, strontium, and calcium hyponitrites, $\text{Ba}(\text{NO})_2 + 4\text{H}_2\text{O}$; $\text{Sr}(\text{NO})_2 + 5\text{H}_2\text{O}$, and $\text{Ca}(\text{NO})_2 + 4\text{H}_2\text{O}$, are obtained by adding the corresponding nitrates to a strongly alkaline solution of the silver salt. The precipitates are washed with alcohol and ether and dried

on filter paper. The calcium salt is the most stable; it is not decomposed by carbonic anhydride at the ordinary temperature, and loses its water of crystallisation with difficulty. The strontium salt cannot be obtained anhydrous by drying at 100° . All three salts are slightly soluble in water, give an alkaline reaction, and when treated with dilute acids evolve nitrous oxide.

Lead Hyponitrites.—The *basic* salt, $\text{PbO}, \text{Pb}(\text{NO})_2$, which is obtained as a yellowish-white precipitate, on adding lead acetate to an alkaline solution of the sodium salt, can be purified by dissolving it in acetic acid and precipitating with ammonia; when treated with acetic acid, it yields lead acetate and the *normal* salt, $\text{Pb}(\text{NO})_2$, which is a yellow, crystalline powder. Both salts are insoluble in water, but dissolve easily in dilute acids and are precipitated as basic salt by the addition of sodium hydroxide or ammonia. When heated, the basic salt decomposes violently, whilst the normal salt explodes; the basic salt is also quickly decomposed by exposure to light.

Copper hyponitrite, $\text{Cu}(\text{NO})_2, \text{Cu}(\text{OH})_2$, obtained by adding copper sulphate to a solution of the sodium salt and subsequently precipitating by neutralising with ammonia, is a green, amorphous powder insoluble in water, but soluble in dilute acids and ammonia, is stable at 100° , yields copper oxide when strongly heated, and is very hygroscopic.

Silver hyponitrite, $\text{Ag}_2(\text{NO})_2$, separates in small crystals from a solution in concentrated ammonia; it is easily soluble in dilute nitric or sulphuric acid, and in concentrated ammonia, and is at once decomposed by dilute hydrochloric acid into the free acid and silver chloride. It is slowly decomposed on exposure to light, or when heated at 100° ; when heated in the air, or in carbonic anhydride, it yields red vapours of nitrous oxide and becomes black.

The free acid does not set free iodine from potassium iodide, nor does it decolorise a solution of iodine. With bromine, it is quickly oxidised to nitric acid, but the reaction is not a quantitative one, and with the calcium, barium, strontium and silver salts from 7.0 to 7.8 atoms of bromine are required for 1 mol. of salt.

When treated with potassium permanganate, only one atom of oxygen is absorbed, with formation of the compound $\text{H}_2\text{N}_2\text{O}_3$.

E. C. R.

Hyperborates and Hypertitanates. By PETR G. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 1898, 31, 953—956. Compare this vol., ii, 332).—*Ammonium hyperborate*, $\text{NH}_4\text{BO}_3 + \frac{1}{2}\text{H}_2\text{O}$, is obtained when boric acid is dissolved in aqueous hydrogen peroxide solution (2.5 per cent.) and ammonia is added; and is deposited in colourless isotropic crystals on the addition of alcohol. In the dry state, it is quite stable, and even when kept over sulphuric acid it does not lose ammonia. When treated with dilute sulphuric acid, it gives hydrogen peroxide, but with concentrated acid it gives ozone, and with hydrochloric acid, chlorine. Its aqueous solution readily decomposes and evolves oxygen; this decomposition proceeds more rapidly at 45° , ammonium nitrite being formed. The freshly prepared salt contains $3\text{H}_2\text{O}$, but when kept for 24 hours over sulphuric acid, the salt containing $\frac{1}{2}\text{H}_2\text{O}$ is formed.

Barium hyperborate, $\text{Ba}(\text{BO}_3)_2 + 7\text{H}_2\text{O}$, is obtained by double decom-

position from a saturated solution of the sodium salt cooled to 0° , in the form of a sparingly soluble, flocculent precipitate; it decomposes slowly at the ordinary temperature. The *calcium*, *copper*, and *nickel* salts have also been prepared. Cobalt chloride reacts with the sodium salt evolving oxygen, and yielding cobalt hyperoxide, $\text{CoO}_2 \cdot \text{CoO}$.

Normal sodium peroxide hypertitanate, $\text{Na}_2\text{O}_2 \cdot \text{TiO}_3 + 3\text{H}_2\text{O}$, which is formed when pertitanic anhydride is treated with hydrogen peroxide and sodium hydroxide ($\text{TiO}_3 : \text{NaOH} = 1 : 2$), separates on the addition of alcohol as a heavy oily layer which gradually solidifies to a yellow powder when placed over sulphuric acid. When treated with dilute sulphuric acid, it yields hydrogen peroxide.

Ammonium peroxide hypertitanate, $(\text{NH}_4)_2\text{O}_2 \cdot \text{TiO}_3 \cdot \text{H}_2\text{O}_2$, obtained in a similar manner, forms glistening, yellow prisms, is fairly stable in the dry state, but rapidly decomposes when in solution. When heated over a free flame, it explodes feebly.

Normal barium peroxide hypertitanate, $\text{BaO}_2 \cdot \text{TiO}_3 + 5\text{H}_2\text{O}$, was obtained as a yellow, flocculent precipitate. J. J. S.

Attempt to cause Helium or Argon to pass through Red-hot Palladium, Platinum, or Iron. By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1897, 61, 267).—Unlike hydrogen, neither argon nor helium is able to pass through a thin sheet of palladium, platinum, or iron, even when the latter is strongly heated in the blow-pipe flame. This would imply their inability to form any compound, however unstable, with these metals, or to dissolve in them at a red-heat, and is another proof of their inertness. W. A. D.

Experiments with Helium. By MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1897, 60, 449—453).—On passing a discharge through a Plücker tube containing helium at 3 mm. pressure, and fitted with platinum electrodes, a reddish-yellow glow is produced, which gradually changes, through shades of yellow and green, to the phosphorescent glow characteristic of a vacuum. These colour-changes are due to the gradual absorption of the helium by the platinum sparked on to the walls of the tube; on carefully heating the latter, the helium is evolved, and the colour-changes become visible in the reverse order. When the green glow is most intense, the best defined line is that in the green at $\lambda = 5015.6$; if at this point the gas remaining unabsorbed by the platinum is completely removed by an air-pump, and the tube gently heated, the absorbed portion is evolved, and the greenish glow reproduced. It appears, therefore, that the latter is not due to the more difficultly absorbed fraction of the helium, but must be attributed solely to the lowering of the pressure consequent on the absorption.

Although hydrogen, nitrogen, and carbon compounds, as well as helium, are, more or less easily, absorbed when sparked with platinum electrodes, argon is only taken up in very small quantity; advantage can be taken of this to separate argon from helium, even when the amount of the latter is only 2 per cent. The mixture of gases is circulated during 6 hours, at 3 mm. pressure, by means of a Sprengel's pump, through a Plücker vacuum-tube kept cool by means of a water-jacket; on exhausting, and subsequently heating the vacuum-tube, helium containing only a trace of argon is obtained.

Kayser and Friedländer's statement (*Chem. Zeit.*, 9, 1529), that atmospheric argon is absorbed by platinum electrodes during a discharge and that certain of the helium lines then become visible, is, in the author's opinion, incorrect.

W. A. D.

Barium Sulphide. By A. MOURLOT (*Compt. rend.*, 1898, 126, 643—646).—Crystallised barium sulphide, BaS, is obtained by fusing the amorphous sulphide in the electric furnace with an arc from a current of 900 ampères and 50 volts, or by heating a mixture of the sulphate and carbon in a similar arc for a few minutes. It forms somewhat large, white crystals, with two very distinct planes of cleavage at right angles to one another; sp. gr. about 4·3; hardness, below that of glass. In general properties, the crystallised sulphide resembles the amorphous compound, but it is less readily attacked by air and various reagents. Fluorine attacks it with incandescence in the cold; oxygen attacks it with incandescence on heating. Potassium chlorate, lead peroxide, and other oxidising agents, as well as phosphoric anhydride and phosphorus oxychloride, also attack it with incandescence. When heated with carbon in the electrical furnace, it is converted into the carbide, Ba₂C.

C. H. B.

CopperAmmonium Sulphate and CopperAmmonium Chloride. By LUIGI SABBATANI (*Chem. Centr.*, 1897, ii, 610—611; from *Ann. Chim. Farm.*, 26, 337—350).—The author gives an account of the poisonous properties and the therapeutic application of these salts. After drying in a vacuum under various conditions, the composition corresponded with the formulæ CuSO₄·4NH₃ + H₂O and CuCl₂·4NH₃ + 2H₂O respectively. Both salts lose water and 2NH₃ even at 100—110°, and very readily at 125°. The chloride is less stable than the sulphate, and gives up half its content of ammonia and water of crystallisation on warming, or if kept in a vacuum over sulphuric acid, or when exposed to the air, much more readily than the sulphate. When dried over lime, in presence of ammonia, the chloride loses all its water but no ammonia. The author is of the opinion that the sulphate, like the chloride, may also crystallise with 2H₂O, although only 1H₂O is retained.

E. W. W.

Solubility of Cerium Sulphate in Water. By WILHELM MUTHMANN and H. RÖLIG (*Zeit. anorg. Chem.*, 1898, 16, 450—462).—Pure cerium sulphate, Ce₂(SO₄)₃, yields a clear solution when shaken with ice-cold water. The authors could only obtain three hydrates by dissolving this salt in pure water; they were not able to obtain the hydrates with 6 and 9H₂O. The hydrate with 5H₂O is obtained in neutral solution at temperatures above 74°, and crystallises in beautiful, monoclinic prisms. The hydrate, with 8H₂O, is obtained between 30° and 74°, and crystallises in rhombic pyramids. The hydrate, with 12H₂O, is obtained by dissolving 20 parts of the sulphate in ice-cold water and separates in very slender needles.

The solubility of the pentahydrate in 100 parts of water varies from 0·775 parts at 100° to 8·20 parts at 40°. Below 40°, it is converted into the octohydrate. The solubility of the octohydrate varies from 19·10 parts at 0° to 4·24 parts at 70°. The solubility of the dodeca-

hydrate varies from 21.40 parts at 0° to 16.22 parts at 25°. Above 25°, it is converted into the octohydrate. Curves of the solubilities are given in the original paper.
E. C. R.

Atomic Weight of Aluminium. By JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1897, 15, 447—453).—The method adopted by the author for determining the atomic weights of oxygen and hydrogen (Abstr., 1896, ii, 244), by dissolving a known weight of aluminium in potassium hydroxide, and determining the weight of the hydrogen evolved, by the difference in weight of the apparatus before and after the dissolution of the hydrogen, and also by determining the increase in weight brought about by burning the evolved hydrogen in pure oxygen, affords a means of determining at the same time the atomic weight of aluminium. Corrections must, however, be applied on account of the impurities contained in the aluminium, and the contraction in volume attending the dissolution of the metal. The corrected values for the atomic weight are $\text{Al} = 26.770$ ($\text{H} = 1$), or $\text{Al} = 26.992$ ($\text{O} = 16$). These numbers do not depend one on the other, but each represents the result of a direct determination by means of which the atomic weight of aluminium is referred to that of the standard element.
H. C.

Aluminium Nitride. By LÉON FRANCK (*Chem. Zeit.*, 1897, 21, 263. Compare Mallet, Trans., 1876, 340; Moissan, Abstr., 1894, ii, 450).—Aluminium nitride is obtained when an intimate mixture of finely divided aluminium and calcium carbide is heated in a porcelain crucible with access of air, by the aid of a blow-pipe. A product obtained in this way was found to contain 15—20 per cent. of nitrogen. It is very slowly decomposed by moist air, somewhat more rapidly by boiling water, and most readily by alkalis, evolving its nitrogen as ammonia. A better yield may be obtained by passing nitrogen over the above mixture, or over a mixture of aluminium and dry calcium hydroxide. It is considered probable that substances so rich in nitrogen may be of use as fertilisers.
J. J. S.

Atomic Weight of Cobalt. By THEODORE WILLIAM RICHARDS and GREGORY PAUL BAXTER (*Zeit. anorg. Chem.*, 1898, 16, 362—376).—The authors have determined the atomic weight of cobalt from the ratio of cobalt bromide to silver bromide and to silver. The methods employed for obtaining the cobalt bromide in a perfectly dry state, and for weighing the same, are similar to those already employed in the case of nickel (Richards and Cushman, this vol., ii, 228). Full details of the preparation of the materials are given in the original paper. The mean of the first series of 3 experiments gave $\text{Co} = 58.984$; the mean of the second series of 9 experiments gave $\text{Co} = 58.995$; the mean of the third series of 8 experiments gave $\text{Co} = 58.987$ (taking $\text{O} = 16$, $\text{Ag} = 107.93$). The atomic weight of cobalt is therefore 58.99 ($\text{O} = 16$) or 58.55 ($\text{O} = 15.88$).
E. C. R.

Tetramminecobalt Sulphite. By KARL A. HOFMANN and S. REINSCH (*Zeit. anorg. Chem.*, 1898, 16, 377—397).—Cobalt acetate is dissolved in 7 per cent. ammonia, and the solution allowed to remain

exposed to the air until it becomes deep violet ; it is then saturated with sulphurous anhydride, and the amorphous, brown precipitate separated and washed with sulphurous acid ; after drying over sulphuric acid, the precipitate has the composition $\text{Co}_2(\text{SO}_3)_3(\text{NH}_3)_2 + 5\text{H}_2\text{O}$ or $3\text{H}_2\text{O}$. It is sparingly soluble in water, and yields cobalt hydroxide when treated with sodium hydroxide. When boiled with 7 per cent. ammonia, it is converted into the compound $\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2\text{NH}_4$, which crystallises in brown plates, is sparingly soluble in water, is decomposed by boiling water, and when treated with hydrochloric acid is converted into the tetrammineroseochloride and a small quantity of praseochloride. The sulphite group cannot be detected by the ordinary reactions.

The group SO_3NH_4 in these compounds is easily replaced by the thiocyanogen, cyanogen, and hydroxyl groups. The compound $\text{Co}(\text{NH}_3)_4(\text{SO}_3)\text{CNS} + 2\text{H}_2\text{O}$, obtained by warming the preceding ammonium compound with ammonium thiocyanate, crystallises in brownish-yellow leaflets, turns red when dehydrated at 80° over sulphuric acid, and is decomposed by boiling with water. When treated with fuming hydrochloric acid, it yields the praseochloride, and with concentrated sulphuric acid it yields a brownish-red solution which quickly changes to violet. When shaken with silver oxide and water, it is converted into the compound $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}]\text{SO}_3\text{OH} + 2\text{H}_2\text{O}$, which is a reddish-yellow, crystalline powder sparingly soluble in water. When the thiocyanate derivative is treated with potassium cyanide, it yields the compound $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}]\text{SO}_3\text{CN} + \text{H}_2\text{O}$.

Vortmann and Magdeburg have obtained a compound which is apparently identical with the authors' aquopentamminecobalt sulphite, by dissolving roseocobalt chloride and ammonium hydrogen sulphite in dilute ammonia. It is obtained in lustrous, brownish-yellow leaflets, together with the tetramminecobalt ammonium sulphite, and is much more soluble in dilute ammonia than the latter, which is easily converted into the aquopentammine sulphite by prolonged digestion with an ammoniacal solution of ammonium sulphite.

Aquopentamminecobalt sulphite, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{SO}_3)_3 + \text{H}_2\text{O}$, crystallises in lustrous, monosymmetric plates ; it is also obtained, together with the sparingly soluble aquotetramminecobalt ammonium sulphite, by digesting carbonatotetramminecobalt chloride with ammoniacal ammonium sulphite. When treated with fuming hydrochloric acid, it yields a brownish-yellow solution, then a red, crystalline powder (probably tetrammineroseochloride) and a violet solution. With concentrated sulphuric acid, it gives a beautiful, ruby-red solution.

The compound, $[\text{Co}_2(\text{NH}_3)_9\text{H}_2\text{O}]3\text{SO}_3 \cdot 2\text{H}_2\text{O}$, is obtained by allowing an ammoniacal solution of cobalt acetate to remain exposed to the air for 2—3 days, and then treating it with sulphurous anhydride, taking care that an alkaline reaction is maintained ; the yellowish-brown precipitate is boiled with ammonia, and the filtrate allowed to crystallise. It forms slender, brownish-yellow needles, and is easily soluble in warm water ; with fuming hydrochloric acid, it gives an intense red solution, which deposits a crystalline mixture of praseochloride and aquotetrammine chloride ; with sulphuric acid, it gives a red solution which quickly changes to bluish-red.

When treated with aqueous ammonium thiocyanate, the last two com-

pounds described above yield the compound $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}]\text{SO}_3\text{CSN} + \text{H}_2\text{O}$, which is identical with the thiocyanate described above. When treated with potassium cyanide, they yield the compound $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}]\text{SO}_3\text{CN} + \text{H}_2\text{O}$; this crystallises in reddish-yellow, rhombic tablets, is decomposed by boiling water, and when treated with fuming hydrochloric acid is converted into the compound $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}]\text{CN}, \text{Cl}_2$; when the latter is treated with silver nitrate, the chlorine is completely eliminated, but not the cyanogen.

The compound $[\text{Co}_2(\text{NH}_3)_9\text{H}_2\text{O}]\text{3SO}_3 + 2\text{H}_2\text{O}$, when treated with sodium nitrite and ammonium chloride, yields the compound $\text{Co}(\text{NH}_3)_4\text{SO}_3\cdot\text{NO}_2$, as a yellow, crystalline powder, which is sparingly soluble in water, and when treated with fuming hydrochloric acid yields praseoehloride.

Aquotetramminecobalt ammonium sulphite,
 $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}]\text{SO}_3\cdot\text{SO}_3\text{NH}_4 + 2\text{H}_2\text{O}$,
 which is obtained from the carbonatotetrammine chloride by digesting it for some days with ammoniacal ammonium sulphite, crystallises in brown prisms; with fuming hydrochloric acid it yields a greenish-yellow solution which gradually becomes green and then blue, and deposits red crystals of the aquotetrammine chloride.

Sulphitotetramminecobalt sodium sulphite, $\text{Co}(\text{NH}_3)_4\text{SO}_3\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$, is obtained by digesting Jörgensen's carbonatotetrammine chloride with an ammoniacal solution of sodium hydrogen sulphite; it crystallises in yellowish-brown leaflets, is easily soluble in water, and gives a reddish-violet solution with concentrated sulphuric acid.

When carbonatotetrammine chloride is boiled with ammoniacal sodium sulphite, it yields the compound $[\text{Co}(\text{NH}_3)_3\text{2H}_2\text{O}]\text{SO}_3\cdot\text{SO}_3\text{Na}\cdot 5\text{H}_2\text{O}$, which crystallises in dark-yellow, rhombic crystals; with fuming hydrochloric acid it yields a brownish-yellow coloration which changes to green, and with concentrated sulphuric acid, a reddish-yellow solution which quickly changes to violet.

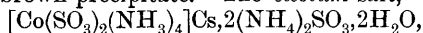
E. C. R.

Constitution of Inorganic Compounds. By ALFRED WERNER and H. GRÜGER (*Zeit. anorg. Chem.*, 1898, 16, 398—423).—Sulphitopentammine and sulphitotetrammine salts are obtained by adding more or less of a solution of sodium hydrogen sulphite to a solution prepared by passing air for 7 to 8 hours through a mixture of 20 grams of cobalt carbonate dissolved in dilute hydrochloric acid to which 100 grams of ammonium carbonate, 500 grams of water, and 250 grams of concentrated ammonia have been added.

Sulphitopentamminecobalt sulphite, $[\text{CoSO}_3(\text{NH}_3)_5]\text{2SO}_3 + 2\text{H}_2\text{O}$, is obtained by adding 10—12 grams of sodium hydrogen sulphite to 500 c.c. of the above solution. After remaining 2—3 days, crystals of disulphitotetramminecobalt ammonia are deposited, and after another 3 days the crystals of the pentammine salt begin to separate; it crystallises in brown tablets and is easily soluble in warm water. The *chloride*, $[\text{CoSO}_3(\text{NH}_3)_5]\text{Cl}$, is obtained by treating the sulphite with the theoretical quantity of concentrated hydrochloric acid; it is a well crystallised salt, easily soluble in water and is precipitated by hydrochloric acid and alcohol. It is unstable in aqueous solution, but quite stable when dry, and when treated with sodium hydrogen sulphite it

yields a crystalline double salt. The *hydrochloride* $[\text{CoSO}_3\text{H}(\text{NH}_3)_5]\text{Cl}_2$, is obtained by treating finely powdered sulphitopentamminecobalt chloride with concentrated hydrochloric acid and then washing out the excess of acid with anhydrous alcohol; it is a carmine, crystalline powder which, on exposure to damp air, quickly decomposes into sulphitopentamminecobalt chloride. The *bromide* separates in brownish-red crystals, the *nitrate* in small, brown crystals. The *double salt with sodium sulphite*, $[\text{CoSO}_3(\text{NH}_3)_5]_2\text{SO}_3 + 2\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$, is obtained by treating the chloride with sodium hydrogen sulphite until the colour changes to yellow; on adding a small quantity of alcohol to the solution, it crystallises in bright yellow leaflets, easily soluble in water; it decomposes when exposed to the air.

Disulphitetetramminecobalt ammonia, $[\text{Co}(\text{SO}_3)_2(\text{NH}_3)_4]\text{NH}_4 + 3\text{H}_2\text{O}$, is obtained by adding a larger quantity of sodium hydrogen sulphite to the above oxidised solution; it crystallises in large, dark brown crystals, is easily soluble in warm water, decomposes slowly in solution, and when treated with alkalis yields the corresponding alkali salts with evolution of ammonia; its aqueous solution yields insoluble precipitates with the salts of the alkaline earths, mercury, silver, and gold. It dissolves in concentrated sulphuric acid, with evolution of sulphurous anhydride, and on adding hydrochloric acid to the solution the green praseo-salt is precipitated. The *sodium salt*, $[\text{Co}(\text{SO}_3)_2(\text{NH}_3)_4]\text{Na} + 2\text{H}_2\text{O}$, obtained by saturating the oxidised cobalt solution with solid sodium hydrogen sulphite, crystallises in small, golden-yellow leaflets, and decomposes when allowed to remain in aqueous solution. The *potassium salt* crystallises in dark yellow needles, the *rubidium salt* in bright brown needles. The *lithium double salt with ammonium sulphite*, $2[\text{Co}(\text{SO}_3)_2(\text{NH}_3)_4]\text{Li}(\text{NH}_4)_2\text{SO}_3$, obtained by treating the ammonium salt with lithium hydroxide in the absence of carbonic anhydride, crystallises in small, brownish-yellow, lustrous leaflets; it is easily soluble in water but quickly decomposes, with the formation of an insoluble brown precipitate. The *cæsium salt*,



obtained in a similar manner to the lithium salt, crystallises in small, dark brown aggregates, is very soluble in water, and quickly decomposes when kept.

The silver, gold, mercury, barium, cadmium, and copper salts of disulphitetetramminecobalt are also described. E. C. R.

Inorganic Hydroxylamine Compounds. By KARL A. HOFMANN and VOLKMAR KOHLSCHÜTTER (*Zeit. anorg. Chem.*, 1898, 16, 463—474).—The compound $\text{HO}\cdot\text{Ca}\cdot\text{O}\cdot\text{NH}_2$ is obtained by digesting finely powdered lime or calcium carbide with a solution of hydroxylamine in methylic alcohol; it is a white powder, is partially decomposed by water at the ordinary temperature into calcium hydroxide and hydroxylamine, and at once reduces Fehling's solution and ammoniacal silver nitrate.

Hydroxylamine ammonium tungstate, $\text{NH}_4\cdot\text{O}\cdot\text{WO}_4\cdot\text{NH}_4$, is obtained by treating finely powdered sodium paratungstate with an aqueous solution of hydroxylamine hydrochloride, and then dissolving the product in 15 per cent. ammonia; it crystallises in thick tablets when

the solution is allowed to evaporate over potassium hydroxide, and at once reduces Fehling's solution and ammoniacal silver nitrate.

The compound $\text{NH}_4 \cdot \text{HPO}_3 \cdot \text{NH}_4\text{O}$, is obtained by neutralising phosphorous acid with ammonia, then adding four times the quantity of ammonia and twomolecular proportions of hydroxylamine hydrochloride to 1 of the acid; after remaining one hour, the solution is precipitated with alcohol and the product recrystallised from absolute alcohol. It is also obtained by heating diammonium phosphite, $\text{HPO}_3(\text{NH}_4)_2$, with hydroxylamine hydrochloride in absolute alcohol and dissolving out the excess of hydroxylamine hydrochloride from the product by warming it with methylic alcohol. It crystallises in slender, white needles, and at once reduces Fehling's solution and ammoniacal silver nitrate.

The compound $\text{HPO}_3(\text{NH}_4\text{O})_2$ is obtained by mixing an aqueous solution of disodium phosphite with 3 molecular proportions of hydroxylamine hydrochloride, and after crystallising out the sodium chloride by evaporation in a vacuum over sulphuric acid, the gummy residue is crystallised from absolute alcohol; it crystallises in long, colourless needles, burns, when heated, with a green flame and evolution of hydrogen phosphide, and quickly reduces Fehling's solution and ammoniacal silver nitrate.

The compound $(\text{H}_2\text{PO}_3)_2(\text{NH}_3\text{O})_3\text{K}_2$ is obtained by adding hydroxylamine hydrochloride to a solution of hypophosphorous acid made strongly alkaline with potassium hydroxide and mixed with absolute alcohol and a little ether. It crystallises from absolute alcohol in thin plates, melts at 86° , is easily soluble in water, and when heated at 90° in aqueous solution rapidly evolves hydrogen phosphide. When hydroxylamine hypophosphite is treated with a solution of hydroxylamine and sodium methoxide in methylic alcohol, a crystalline compound is obtained which explodes violently.

Metavanadic acid, VO_3H , yields three crystalline products with hydroxylamine namely, $\text{VO}_6\text{N}_5\text{H}_{16}$, $\text{VO}_5\text{N}_4\text{H}_{13}$, and $\text{VO}_6\text{N}_3\text{H}_{10}$. The compound $\text{VO}_3\text{H}(\text{NH}_3\text{O})_2(\text{NH}_3)_2$ is obtained as follows. Strong ammonia (100 c.c.) is saturated at 5° with ammonia and mixed with finely-powdered hydroxylamine hydrochloride (10 grams); the mixture is cooled to 0° and ammonium metavanadate (3 grams) gradually added and the mixture allowed to remain at 0° until yellow crystals separate; the lemon-yellow leaflets thus obtained are washed with strong ammonia and dried in an atmosphere of ammonia over potassium hydroxide at as low a temperature as possible. It is quickly decomposed by water and dilute sodium hydroxide, dissolves in hydrochloric or sulphuric acid with evolution of nitrous oxide, and when heated decomposes with a slight explosion. The compound $\text{VO}_6\text{N}_5\text{H}_{16}$ is obtained in a similar manner to the preceding, but only 1.5 grams of ammonium metavanadate are employed to 10 grams of hydroxylamine hydrochloride; it crystallises in slender yellow needles, is rapidly decomposed by moisture and carbonic anhydride, and contains 1 mol. metavanadic acid, 3 mols. hydroxylamine, and 2 mols. ammonia. The compound $\text{VO}_6\text{N}_3\text{H}_{10}$ is very unstable and was not obtained in a pure state.

The compound $\text{Nb} \cdot \text{O}_6\text{N}_3\text{H}_{10}$, obtained by treating potassium pyro-niobate, $\text{K}_2\text{Nb}_6\text{O}_{19} + 16\text{H}_2\text{O}$, with strong ammonia and hydroxylamine

hydrochloride for some days, is a white powder only slightly soluble in water, and explodes violently with a yellowish flame when heated.

E. C. R.

Decomposition of Auric Chloride in Dilute Solution. By EDWARD SONSTADT (*Chem. News*, 1898, 77, 74).—A solution was prepared containing one part of ordinary auric chloride, dried on the water bath, in 15,000 parts of distilled water that had been coloured with dichromate and redistilled. This solution, on heating for some hours, yielded a precipitate of gold, whilst hydrogen peroxide was detected in the solutions. The change is expressed by the equation $\text{AuCl}_3 + 2\text{H}_2\text{O} = \text{AuCl} + 2\text{HCl} + \text{H}_2\text{O}_2$, the aurous chloride yielding gold and auric chloride when heated with water. An analogous behaviour of platonic chloride in dilute solutions has already been noted (*Proc.*, 1898, 25).

D. A. L.

Action of Carbonic Oxide on Palladious Chloride. By EDWARD FINK (*Compt. rend.*, 1898, 126, 646—648).—When palladious chloride is heated at 260° in a current of carbonic oxide, a crystalline product is obtained which is red near the hot part of the tube and yellow where it has condensed in the cooler parts of the tube. The crude product, when heated, yields a sublimate of colourless needles, whilst a reddish-brown liquid remains and crystallises in yellow needles on cooling. The yellow substance, when purified by crystallisation from carbon tetrachloride, melts at 132° , and has the composition $2\text{PdCl}_2, 3\text{CO}$. It is decomposed by water in accordance with the equation $2\text{PdCl}_2, 3\text{CO} + 2\text{H}_2\text{O} = \text{CO} + 2\text{CO}_2 + \text{Pd}_2 + 4\text{HCl}$. When heated at about 263° , it loses carbonic oxide and yields a crystalline, yellowish red product, from which, by sublimation in carbonic anhydride, yellow needles of the compound $\text{CO}:\text{PdCl}_2$ are obtained.

The white needles have the composition $\text{PdCl}_2, 2\text{CO}$ and melt at 142° ; at about 218° , they lose carbonic oxide and yield the compound $2\text{PdCl}_2, 3\text{CO}$.

It will be observed that the palladium compounds are analogous to those formed by platinum.

C. H. B.

Mineralogical Chemistry.

Gaseous Constituents of Certain Mineral Substances and Natural Waters. By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1897, 60, 442—448).—The authors have examined the gases evolved when several finely-powdered minerals are heated to a red heat, either alone or with potassium hydrogen sulphate. Samples of fergusonite, monazite, samarskite, and columbite gave from 1.3—1.5 c.c. of helium per gram, whilst pitchblende, from Colorado, gave from 0.27—0.3 c.c. per gram; malacone, ZrSO_4 , from Hitteroe in Norway, contained traces of both argon and helium. Cinnabar and

cryolite gave small quantities of carbonic oxide only, whilst from apatite hydrogen also was obtained; from barytes, celestine and scapolite, no gas was evolved. Hydrogen alone was obtained from serpentine, from the Riffelhorn, and from gneiss from Kashmir, whilst a cobalt ore, containing manganese dioxide, yielded oxygen only. Lava from Iceland gave carbonic anhydride only, whilst the blue clay and the coarse-grained gravel of the Kimberley diamond field yielded hydrogen and carbonic oxide. From five specimens of meteoric iron, hydrogen only was obtained, without a trace of either argon or helium.

A carboy of water from the Old Sulphur Well, Harrogate, yielded 45 c.c. of argon, whilst from the same quantity of water from the Strathpeffer Wells 25 c.c. were obtained. Samples of gas from the Raillière, Des Œufs, César and Espagnol springs at Cauterets, Hautes-Pyrénées, contained both argon and helium. Attempts to separate these gases by diffusion, and by taking advantage of their relative solubilities in water, led to no result. The helium was, however, obtained in a pure state by absorbing it by the platinum electrodes of a vacuum tube (compare this vol., ii, 375), and subsequently liberating the gas by heating the tube.

From their experiments, the authors conclude that no new gaseous element is present in the minerals or natural waters examined.

W. A. D.

Gases enclosed in Crystalline Rocks and Minerals. By WILLIAM A. TILDEN (*Proc. Roy. Soc.*, 1897, 60, 453—457).—A number of rocks and minerals examined by the author gave, on being heated, volumes of gas, varying from that of the mineral taken, to eighteen times this volume; the proportion of hydrogen present varied from 12·49 to 88·42 per cent., and that of carbonic anhydride from 5·50 to 77·72 per cent.; carbonic oxide, nitrogen, and methane were present in smaller proportion, but in no case could helium be detected. The gas is apparently enclosed in microscopic cavities, visible in thin sections of the mineral, but none of it is evolved when the latter is coarsely powdered.

The author accounts for the large proportion of hydrogen and carbonic oxide by assuming that the rock crystallised in an atmosphere rich in carbonic anhydride and steam, and in contact with some easily oxidisable substance, for example carbon, a metal such as iron, or a metallic protoxide. Ferrous oxide, a substance of the latter kind, is oxidised by both steam and carbonic anhydride, at a red heat, to the magnetic oxide, the latter substance remaining completely unaffected under these conditions.

W. A. D.

Melting Points of Minerals. By RALPH CUSACK (*Proc. Roy. Irish Acad.*, 1897, [iii], 4, 399—413).—An improved form of Joly's maldometer (*Abstr.*, 1892, 414) is described. The method forms a convenient means of identifying minerals, and the readings are accurate to 2° of temperature. Most silicates present a greater or less degree of viscosity, and do not seem to fuse at any very definite temperature; quartz softens at 1406°, and is liquid at 1425°, but only runs freely at 1440°. Small variations in composition do not seem to seriously

affect the melting point, as seen, for example, in the pyroxenes and amphiboles. The dimorphous rutile and brookite have the same melting point, whilst for the somewhat allied topaz and kyanite it is very different. The following are the extreme values obtained for samples from different localities.

Actinolite ... 1272—1288°	Almandine 1263—1268°	Adularia ... 1164—1168°	Zincite 1260°
Tremolite ... 1219—1223	Idocrase... 1024—1035	Albite 1172	Cassiterite 1127
Hornblende 1187—1200	Epidote ... 954—9766	Microcline 1169	Rutile 1560
Diopside ... 1187—1195	Zoisite ... 995	Labradorite 1223—1235	Brookite ... 1560
Diallage..... 1264—1300	Diophtase... 1171	Tourmaline 1012—1102	Uraninite... 1188
Augite 1187—1199	Axinite ... 995	Kyanite ... 1090	Vivianite ... 1114
Spodumene 1173	Meionite 1281	Sphene ... 1127—1142	Apatite..... 1221—1227
Eustatite ... 1295	Nepheline 1059—1070	Staurolite 1115	Molybdenite 1185
Wollastonite 1203—1208	Sodalite ... 1127—1133	Andalusite 1209	Galena 727
Olivine 1363—1378	Leucite ... 1298	Cuprite ... 1162	Blende 1049

The melting points of topaz, zircon, corundum and wavelite are higher than that of platinum, and therefore cannot be determined by this method.

L. J. S.

Composition of Nova Scotia Coals and other Minerals. By E. GILPIN, jun. (*Trans. Nova Scotian Inst. Sci.*, 1897, 9, 246—254).—Analyses are given of several coals, iron pyrites, and iron ores.

L. J. S.

Products of Decomposition of Pyrites in the Paris Basin. By ALFRED LACROIX (*Bull. Soc. fran. Min.*, 1897, 20, 288—308).—In the Paris basin, pyrites and marcasite occur in chalk, Eocene clays, lignite, &c. Two main types of alteration may be distinguished as the “hepatic” and the “saline.” In the former, the product, limonite or hæmatite, preserves the original form of the mineral. In the latter, the pyrites is more rapidly oxidised in the presence of air to melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and sulphuric acid. By the action of these on the various rocks, secondary products are formed. Sulphuric acid acting on limestone and clay gives gypsum and websterite, $\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 9\text{H}_2\text{O}$, respectively. Melanterite and sulphuric acid, in acting on limestone, give gypsum and chalybite, and on clay, halotrichite, $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$. By the oxidation of the melanterite, copiapite, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 + 18\text{H}_2\text{O}$, is formed, and this by its action on limestone gives apatelite, $4\text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 3\text{H}_2\text{O}$, and gypsum. Similar reactions take place in the island of Naxos and at Sasaki in the Gulf of Corinth (*Abstr.*, 1897, ii, 508).

L. J. S.

Berthierite from Bohemia. By ADOLF HOFMANN (*Sitz.-ber. k. böhm. Ges. d. Wiss.*, 1898, *Jahrg.* 1897, 2, No. xlix, 3 pp.).—The mineral veins at Bohutin, near Příbram, when in diabase, contain calcite and argentiferous galena, and when in the grauwacke they contain quartz, pyrrhotite and native silver, but those in connection with the more rarely occurring quartz-mica-diorite contain much stibnite. In the last of these berthierite occurs, and the succession of minerals is: chalybite, galena, quartz, stibnite, berthierite, quartz, barytes, galena. The berthierite occurs as fine needles intergrown with quartz and stibnite; from the latter it is easily distinguished by its reddish tarnish. The fractured surfaces are dark steel-grey. Analyses by R. Vamvera gave I and II.

	Sb.	Fe.	S.	Pb.	Quartz.	Total.	Sp. gr.
I.	45·60	10·62	23·16	trace	19·76	99·14	3·89—3·91.
II.	42·49	11·04	23·16	trace	23·31	100·00	
III.	56·42	13·89	29·69	—	—	100·00	

After deducting quartz, which is seen as microscopic enclosures, the mean (III) of these agrees closely with the formula $\text{FeS, Sb}_2\text{S}_3$.

L. J. S.

Kalgoorlite, a new Telluride from Western Australia. By EDWARD F. PITTMAN (*Records Geol. Survey N.S.W.*, 1898, 5, 203—204. Compare Abstr., 1897, ii, 503).—The tellurides of Kalgoorlie occur as veins, splashes, and pockets, in dykes of a schistose quartz-felsparporphyry. A massive, iron-black mineral with sub-conchoidal fracture gave analysis I, by J. C. H. Mingaye, formula, $\text{HgAu}_2\text{Ag}_6\text{Te}_6$; to this the name kalgoorlite is given. The amalgam found in the district may have been produced by the decomposition of this mineral.

	Au.	Ag.	Hg.	Cu.	S.	Te.	Total.	Sp. gr.
I.	20·72	30·98	10·86	0·05	0·13	[37·26]	100·00	8·791.
II.	41·76	0·80	—	—	—	56·65	99·21	9·377.

A pale yellow mineral, also from Kalgoorlie, is shown by analysis II to be probably calaverite.

L. J. S.

Tellurium in Gold-ores from South Dakota. By FRANK CLEMES SMITH (*Trans. Amer. Inst. Mining Eng.*, 1897, 26, 485—515).—The so-called refractory gold-ores of the Potsdam sandstone in the Black Hills, South Dakota, have been found in all cases to contain tellurium. The blue unoxidised sandstone ore contains pyrites, gypsum, and fluorite; the oxidised ore is red. The average of several assays, which show a few ounces to the ton, gives I as the composition of the telluride. An assay of the richer telluride ore from Cripple Creek, Colorado, gave II. Both these agree in composition with sylvanite.

	An.	Ag.	Te.	Total.
I.	7·64	32·39	59·96	100·00
II.	5·61	34·23	60·16	100·00

The methods of assaying these ores are described in detail, and their metallurgical treatment discussed.

L. J. S.

[Bismuth Telluride, Apatite and Minervite from N. S. Wales.] By JOHN C. H. MINGAYE (*Ann. Rept. for 1896, Dept. Mines, N.S.W.*, 1897, 20—21) and by GEORGE W. CARD (*Records Geol. Survey N.S.W.*, 1897, 5, 66).—In the report, various technical analyses of rocks, clays, waters, coals, ores, &c., are given, together with analyses of the following minerals, short descriptions of which are given in the second paper.

Bismuth telluride from Slippery Creek, near Oberon. This occurs with free gold in quartz, and is associated with the greenish-yellow alteration product, montanite. A partial analysis gave

Bi.	Te.	S.	Gangue.	Se, Au, Ag.
70·82	19·59	4·69	0·06	Nil,

Apatite from Gordon Brook. Pinkish-white, hexagonal crystals occurring with actinolite in veins traversing granite. The mean of two analyses is

CaO.	P ₂ O ₅	Ca. (?)	Cl.	F.	MgO.	Fe ₂ O ₃ .	Gangue.	H ₂ O.	Total.
48.68	41.16	3.82	1.30	2.89	0.20	0.74	1.28	0.29	100.36

The gangue contained SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, and traces of P₂O₅.

A white, earthy mineral from the Jenolan Caves has much the same composition as minervite (Abstr. 1893, ii, 419, 577; 1896, ii, 529). The mean of two analyses is

Al ₂ O ₃ .	K ₂ O.	Fe ₂ O ₃ .	P ₂ O ₅ .	Insol.	H ₂ O at 200°.	H ₂ O above 200°.	Total.
20.59	8.95	0.19	40.85	1.09	9.58	18.21	99.46

Also traces of CaO and MgO, but no F, Cl, or SO₃. The associated clay contains some phosphoric acid. L. J. S.

Solution of Silica under Atmospheric Conditions. By C. WILLARD HAYES (*Bull. Geol. Soc. Amer.*, 1897, 8, 212—220).—Several cases are cited in which quartz pebbles in conglomerates are etched down to the general level of the exposed rock surface. The dissolution of the quartz is attributed to the combined action of azo-humic acids and alkali carbonate solutions. Thenard (*Compt. rend.*, 1870, 70, 1412) has shown that simple humic acid dissolves only 8 per cent. of silica, whilst azo-humic acid combines with 7 to 24 per cent., depending on the content of nitrogen; the compounds thus formed are easily soluble in alkali carbonates, forming alkali salts of the silico-azo-humic acids. L. J. S.

"Fresh-water Chalk" from Essex. By THOMAS S. DYMOND and FRANK W. MARYON (*Essex Naturalist*, 1897, 10, 213—215).—A soft, white, granular substance forms a bed either in or upon glacial drift at Halstead. Analysis of material dried at 100° gave

CaO.	MgO.	Fe ₂ O ₃ , Al ₂ O ₃ .	P ₂ O ₅ .	CO ₂ .	SiO ₂	H ₂ O and organic matter.	Total.
54.250	Nil	0.563	0.127	42.625	1.200	1.530	100.295

Since remains of organisms were not detected, the material has probably been directly deposited from water owing to loss of carbonic anhydride. L. J. S.

Barytes Nodules in Wood. By ELLSWORTH B. KNERR (*Trans. Kansas Acad. Sci.*, 1898, 15, 80—81).—In digging a well near Midland College, bits of wood were met with at a depth of 40 feet. In this wood are numerous white spheres $\frac{3}{8}$ — $\frac{1}{8}$ inch diam., with an internal radiated structure. Analysis proved the material to be barytes.

SO ₃ .	BaO.	CaO.	SiO ₂ and gangue.	Total.	sp. gr.
33.25	62.17	0.50	4.00	99.92	4.55

L. J. S.

Aluminite from the Salt Range. By H. H. HAYDEN (*Records Geol. Survey India*, 1897, 30, 110)—Aluminite, which has not before been known from India, occurs as veins in the shale underlying the coal seam at Chittidand, in the Salt Range. It has a chalky appear-

ance, and under the microscope is seen to consist of small, monosymmetric crystals. $H=1-2$; sp. gr. (of impure material) = 1.707. Selected material gave, on analysis,

Al_2O_3 .	SO_3 .	H_2O .	CaO, ZnO, Fe_2O_3 .	Total.
30.08	23.63	46.44	traces	100.15

This agrees with the usual formula, $Al_2O_3, SO_3, 9H_2O$. L. J. S.

Deposit in Delaval Colliery, Northumberland. By CHARLES J. MURTON and SAVILLE SHAW (*Trans. Fed. Inst. Min. Eng.*, 1895, 10, 67-71; and *Trans. N. Engl. Inst. M. E.*, 1895, 45, 67).—On a floor of under-clay in some very old workings in the Delaval Colliery, Benwell, Northumberland, a deposit of a soft, white material is found. When exposed to the air, this dries and shrinks to a white, opaque, friable mass, which breaks with a conchoidal fracture, and adheres strongly to the tongue. It is infusible, and is readily soluble in warm, dilute hydrochloric acid. Analysis gave

Al_2O_3 .	CaO .	SiO_2 .	SO_3 .	H_2O .	Total.
37.93	1.90	12.12	5.30	42.44	99.69

Water extracts all the calcium, together with a little silica.

The substance is considered to be a mixture of collyrite, aluminite, and a hydrate silicate of calcium, in the proportions $7(2Al_2O_3, SiO_2, 9H_2O) + Al_2(SO_4)_3, 2Al_2O_3, 9H_2O + 2(CaO, SiO_2, 18H_2O)$.

[Aluminite is $Al_2O_3, SO_3, 9H_2O$.] L. J. S.

[Nitratine] from South-west Africa. By HERMANN THOMS and G. BOELLING (*Chem. Centr.*, 1897, ii, 57, 1113; from *Ber. Deutsch. pharm. Ges.*, 1897, 7, 168-170. Compare *Abstr.*, 1896, ii, 529).—A mineral, locally known as "Klipzweet" or "Boomester," occurs as an efflorescence on the undersides of overhanging rocks in the Kharas Mountains and on the Orange River, in Namaqualand, German S.W. Africa. Analysis gave

K_2O .	Na_2O .	CaO .	Fe_2O_3 .	N_2O_5 .	Cl .	H_2O .	SiO_2 .	SO_3 .
10.39	27.86	1.10	0.46	38.56	10.54	2.74	7.12	2.88

It is, therefore, an impure nitratine, containing 60.71 per cent. of sodium nitrate. L. J. S.

Mossite, and the Crystalline Form of Skogbolite. By WALDEMAR C. BRÖGGER (*Vidensk. Skrifter, I. Math.-nat. Klasse, Kristiania*, 1897, No. 7, pp. 1-19).—The new mineral, mossite, occurs with yttrantalite and columbite in a pegmatite vein at Berg in the parish of Råde, near Moss, in Norway. The tetragonal crystals are black with sub-metallic lustre; $a:c=1:0.64379$; they are usually twinned on (101) and elongated in the direction of the pyramid edge [111, $\bar{1}\bar{1}1$], then having the appearance of simple orthorhombic crystals of prismatic habit. Analysis by G. Thesen gave

Nb_2O_5 .	Ta_2O_5 .	SnO_2 .	FeO .	$Al_2O_3, MnO, \&c.$	Total.	Sp. gr.
31	52	0.18	16.62	Nil	99.72	6.45
82.92						

This gives the formula $\text{FeNb}_2\text{O}_6, \text{FeTa}_2\text{O}_6$. Mossite and tapiolite are therefore to be considered as the tetragonal equivalents of columbite and tantalite respectively. Crystals of tapiolite from Sukula, in Finland, present the same habit and twinning as mossite; $a : c = 1 : 0.65251$.

The so-called tantalite from Tammela, in Finland (= "Tammela-tantalite" = skogbölite), is shown to be identical with tapiolite. The crystals of this iron tantalate (FeTa_2O_6), which were described as orthorhombic with a form more or less closely related to that of columbite, are shown to be really tetragonal and twinned like mossite; $a : c = 1 : 0.65189$.

The following substances form a homeomorphous group: mossite, tapiolite, dechenite?, AgClO_3 , AgBrO_3 , xenotime, acid phosphates and arsenates of ammonium and potassium, rutile, cassiterite, &c.; and there is a double homeomorphism shown by rutile and brookite with mossite and columbite.

L. J. S.

Synthesis of Perovskite and Pyrochlore Minerals. By PER JOHAN HOLMQUIST (*Bull. Geol. Inst. Upsala*, 1897, 3, 181—262).—A detailed summary is given of the literature of perovskite and pyrochlore, and of the minerals related to them, namely, dysanallyte, knopite, koppite, hatchettolite, microlite, pyrrhite and azor-pyrrhite. The various methods which have been successful in the artificial production of any of these minerals, or of related compounds, are also reviewed.

By fusing the pure oxides with sodium fluoride at a high temperature (1500°), and slowly or quickly cooling, the author has obtained the following crystallised compounds.

Tantalalic acid and niobic acid. The flux here used was borax. The crystals are probably orthorhombic. Sp. gr. of the former = 7.777, and of the latter = 4.568. $\text{Na}_2\text{O}, \text{Nb}_2\text{O}_5$, by fusing sodium carbonate and niobic acid with sodium fluoride; pseudo-cubic crystals with optical anomalies; sp. gr. = 4.512—4.559. $2\text{Na}_2\text{O}, \text{Nb}_2\text{O}_5$, by the same method, but with the materials in different proportions; this is decomposed by water.

$\text{Na}_2\text{O}, 3\text{TiO}_2$; orthorhombic needles; sp. gr. = 3.4925—3.508. This is considered to be possibly isomorphous with perovskite, CaO, TiO_2 , since a powder having this composition is absorbed by the needles to the extent of 32.9 per cent. Perovskite is not formed by fusing the oxides with sodium fluoride. When molten sodium and calcium carbonates are poured into fused $\text{TiO}_2 + \text{Na}_2\text{CO}_3$, there is a precipitation of pseudo-cubic perovskite crystals, which show the same optical anomalies as the natural mineral.

$2\text{CaO}, \text{Nb}_2\text{O}_5$; acicular and pseudo-cubic crystals; sp. gr. = 4.484. $3\text{CaO}, \text{Nb}_2\text{O}_5$ with part of the calcium replaced by sodium; pseudo-cubic. $2\text{CaO}, \text{Ta}_2\text{O}_5$; pseudo-cubic. Most of the above calcium salts are pseudo-cubic, some are also orthorhombic, and probably represent dimorphous forms. $5\text{ThO}_2, 16\text{Nb}_2\text{O}_5$ and $\text{ZrO}_2, 5\text{Nb}_2\text{O}_5$ (Abstr., 1896, ii, 564) are also described.

Pyrochlore and dysanallyte; colourless isotropic octahedra with the composition $\text{NaCaNb}_2\text{O}_6\text{F}$; sp. gr. = 4.196—4.290; index of

refraction for sodium light, 2·149. When this was heated to a higher temperature and slowly cooled, octahedral and pseudo-cubic crystals were formed; the latter had a sp. gr. = 4·122—4·399, and composition $3(\text{Na}_2\text{O}, \text{Nb}_2\text{O}_5), 2(2\text{CaO}, \text{Nb}_2\text{O}_5)$, thus corresponding with a sodium-calcium-dysanallyte. Under the same conditions, but with the presence of some iron and manganese, yellow, isotropic octahedra of pyrochlore and black, shining cubes of dysanallyte were produced; these differ somewhat in composition from the preceding, and there seems to be isomorphous replacement between them. In the presence of cerium, brown octahedra of koppite were obtained, together with dysanallyte. A uranium pyrochlore (hatchettolite) was prepared as isotropic octahedra; this has the composition $7(\text{Na}_2\text{O}, \text{Nb}_2\text{O}_5) + 2(2\text{UO}_2, \text{Nb}_2\text{O}_5)$. From the analysis of these products, resembling pyrochlore and dysanallyte, complicated formulæ are given. Twinned tetragonal crystals related to microlite were also prepared.

The chemical constitution, and the nature of the optical anomalies of these salts and minerals, is discussed in detail; between the pseudo-cubic and the orthorhombic members, a crystallographic relation can be traced.

The composition of natural pyrochlore is discussed, and the following new analysis given of the Alnö mineral; sp. gr. = 4·348 (compare Abstr., 1895, ii, 509).

Nb_2O_5 .	TiO_2 .	ZrO_2 .	Ce_2O_3 .	FeO .	CaO .	Na_2O .	K_2O .	F .	H_2O .	Total
65·29	2·85	2·58	5·03	1·10	16·20	6·29	0·37	4·08	0·44	102·51

For this the formula is given as $5(\text{NaCaNb}_2\text{O}_6\text{F}) + 2(\text{NaCa}_2\text{Nb}_2\text{O}_7\text{F}) + \text{CaTiO}_3 + 2\text{CaO}, \text{Nb}_2\text{O}_5$,
L. J. S.

Chloritoid from Kincardineshire. By GEORGE BARROW (*Quart. Journ. Geol. Soc.*, 1898, 54, 149—156).—Minute, dark, glistening crystals of chloritoid occur in a spotted schist at Drumtochty, near Fordun, and at other localities in Kincardineshire; they are hard and brittle, have a rudely hexagonal outline, and are dark green by transmitted light. Under the microscope, they are seen to have jagged edges, and to be intergrown with, and enclose, quartz, chlorite, and mica. Twinning is frequent, and there is a fairly well-marked basal cleavage. The pleochroism is strong, the colour varying from green to indigo-blue; optically positive, with high index of refraction and low birefringence. The collection of pure material was a matter of some difficulty; four analyses showed a decrease in silica and alkalis, as the material was increased in purity; the most pure gave,

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MgO .	Mn.	Alkalis.	Loss on ignition.	Total.
26·00	40·05	5·05	19·50	2·88	trace	trace	6·00	99·48

In composition, the mineral agrees closely with the chloritoid, from the Ile de Groix, examined by Barrois. It is suggested that chloritoid and ottrelite, both of which have the same optical characters, may be identical, and that the differences shown in the analyses are due to impurities enclosed in the crystals.
L. J. S.

Manganiferous Conglomerate from Essex. By THOMAS S. DYMOND (*Essex Naturalist*, 1897, 10, 210—212).—Hard, tabular masses of cemented gravel occur on the surface of the London clay in the neighbourhood of Tendring, near Colchester; they are used as building stones. Analysis of the cementing material gave,

SiO ₂ and sand.	MnO ₂ .	MnO.	Fe ₂ O ₃ .	H ₂ O (at 120°)	Ca, Al, &c.	Total.
60·960	6·505	2·840	18·315	7·850	[3·530]	100·000

L. J. S.

Weathering of Micaceous Gneiss in Virginia. By GEORGE P. MERRILL (*Bull. Geol. Soc. Amer.*, 1897, 8, 157—168. Compare Abstr., 1896, ii, 483; 1897, ii, 107).—A highly felspathic gneiss with abundant black mica occurs at North Garden, in Albemarle Co., Virginia; it contains orthoclase, soda-lime feldspars, and quartz, with accessory zircon, iron ores, and apatite, and, in considerable quantity, radiating masses of a soda-potash zeolite. Analysis of the fresh rock gave the results under I; the portion soluble in hydrochloric acid and sodium carbonate solutions gave II. In weathering, the rock becomes brownish and friable, and finally passes into red sand and clay. The decomposed rock gave analysis III; the portion soluble in hydrochloric acid and sodium carbonate solutions, IV; and the insoluble portion, V, this being mainly quartz.

	SiO ₂ in HCl.	Al ₂ O ₃ in Na ₂ CO ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	P ₂ O ₅ .	Loss on ignition.	Total.
I.	60·69	16·89	9·66	4·44	1·06	4·25	2·82	0·25	0·62	100·08.
II.	1·43	8·66	13·54	1·64	0·89	2·40	1·10	0·23	0·62	30·51.
III.	45·31	26·55	12·18	trace	0·40	1·10	0·22	0·47	13·75	99·98.
IV.	0·55	17·14	24·86	11·80	0·06	0·37	0·75	0·25	—	13·40
V.	28·90	1·55	0·22	0·07	0·04	0·31	trace	trace	0·35	31·44.

The loss and gain of the various constituents are calculated on the assumption that the alumina has remained constant (Abstr., 1897, ii, 107); this shows that 44·67 per cent. of the original matter has been leached away, that of the original silica 52·45 per cent. is lost, and that most of the iron remains, whilst most of the lime, magnesia, and alkalis are carried away.

The mode of formation of zeolites in rocks is discussed; they seem to be the results of deep-seated hydrometamorphism, rather than of surface weathering. The occurrence of zeolites in soils is doubted, and the soluble potash, &c., is attributed to the presence of pinites.

L. J. S.

Granite from Königshain. By J. HAZARD (*Chem. Centr.*, 1897, ii, 675; from *Geol. Spezialkarte K. Sachsen, Sektion Löbau-Reichenbach*).—The granite boss of Königshain consists of a medium to coarse grained rock, composed of quartz and felspar with a little mica. The felspars, analysed by A. Becker, are: I, microcline-albite-perthite; II, albite. Albite from the pegmatite gave III.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.
I.	64·52	22·48	0·60	0·96	0·60	1·68	9·40	0·36	100·60.
II.	64·06	18·83	0·52	—	—	12·88	3·07	0·50	99·86.
III.	67·77	19·85	—	—	—	—	12·32	0·12	100·06.

In drusy cavities in the granite are : *æschynite*, *albite*, *anatase*, *aphrosiderite*, *axinite*, *beryl*, *cassiterite*, *chlorite*, *diaspore*, *epidote*, *fergusonite*, *fluorite*, *gadolinite*, *hæmatite*, *magnetite*, *meroxene*, *microcline*, *microcline-albite-perthite*, *molybdenite*, *orangite*, *psilomelane*, *smoky quartz*, *tourmaline*, *wolframite*, *xenotime*, *zinnwaldite*, *zircon*, and *malacone*. The surrounding granites and diorite dykes are altered at the contacts of this granite boss. L. J. S.

Phosphatised Trachyte from Clipperton Atoll. By J. J. HARRIS TEALL (*Quart. Journ. Geol. Soc.*, 1898, 54, 230—232).—On one part of the ring of Clipperton Atoll, in the northern Pacific, is a mass, 60 feet high, of more or less altered trachyte. The least altered rock is brown, and consists of phenocrysts of sanidine set in a ground-mass of microlitic feldspars and brown interstitial matter ; analysis gave the results under I ; the phosphoric acid is present in the brown substance. More altered, white or cream-coloured, material gave II and III.

	SiO ₂ .	P ₂ O ₅ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.
I.	54·0	8·4	17·9	4·4	1·4	4·5	5·0	3·8	99·4.
II.	43·7	17·0	—	—	—	—	—	12·2	—
III.	2·8	38·5	25·9	7·4	(Insoluble 2·2)			23·0	99·8.

These analyses show that the gradual removal of the silica and alkalis is accompanied by the introduction of phosphoric acid and water ; the change has probably been effected by a solution of ammonium phosphate derived from guano (compare *Abstr.*, 1896, ii, 185). Examination of microscopic sections shows that the phosphatising process first attacks the interstitial matter, then the microlitic feldspars, and last of all the porphyritic sanidines. Under a high power, the secondary substance shows a concretionary or agate-like structure. The composition shown in analysis III is similar to that of Shepard's redondite, from Redonda in the West Indies ; specimens from this place show the structure of an andesite. L. J. S.

Meteoric Irons. By EMIL W. COHEN (*Ann. k.k. naturhist. Hof-museums, Wien*, 1897, 12, 119—126).—*Nedagolla*, Vizagapatam district, Madras. This is one of the few siderites, and the only ataxite, of which the fall has been observed ; it fell on January 23rd, 1870. The structure is granular, like that of the Locust Grove and Forsyth Co. irons (*Abstr.*, 1897, ii, 272, 416). Analysis gave the results under I.

Primitiva, Tarapaca, Chili.—This iron has also the granular structure of an ataxite ; schreibersite and graphite are present. Analysis of material freed as far as possible from schreibersite gave II. Chromium and chlorine are absent.

Newstead, Roxburgshire, Scotland.—This iron was found in 1827 at a depth of 3 or 4 feet in a stratum of clay ; its meteoric origin has been doubted, and the present author comes to the conclusion that it is artificial. The iron is very brittle, and the microscopic structure resembles that of steel ; it also differs from meteoric iron in the high percentage of carbon, and in the absence of nickel and cobalt (analysis

III). Thomson's analysis of 1862 is quoted under IV. Analyses I—III by O. Sjöström.

	Fe.	Ni.	Co.	Cu.	P.	S.	C.	SiO ₂ .	Total.	Sp. gr.
I.	92·61	6·20	0·49	trace	0·02	0·05	—	0·25	99·62	7·8613
II.	94·72	4·72	0·71	trace	0·18	0·02	0·03	—	100·38	—
III.	96·01	nil.	nil.	—	0·22	0·15	2·96	0·82	100·16	7·0691
IV.	93·51	4·86	—	—	—	—	0·59	0·91	99·87	—

L. J. S.

Water of the Lower Amazon. By FRIEDRICH KATZER (*Sitz.-ber. k. böhm. Ges. Wiss.*, 1898, *Jahrg.* 1897, 1, No. XVII, pp. 1—38).—Several analyses are given of water taken from the Amazon at various points between Obidos and the mouth. The water contains an unusually small amount of soluble constituents, and in this respect the Amazon is one of the purest rivers in the world.

L. J. S.

Kansas Mineral Waters. By HERBERT E. DAVIES (*Trans. Kansas Acad. Sci.*, 1898, 15, 82—88); and by ELLSWORTH B. KNERR (*ibid.*, 88—89).—In these papers, several analyses are given of mineral waters from Kansas.

L. J. S.

Iodine Spring at Wels. By EUGEN LUDWIG (*Chem. Centr.*, 1897, i, 718; from *Wien klin. Woch.*, 1897, 10, 56—57).—Mineral water issues, at the rate of 48 hectolitres in 24 hours, from a boring 500 m. deep at Wels, in Upper Austria. The Miocene strata, through which the upper part of the boring passes, yield an inflammable gas. The water is ferruginous and becomes cloudy in contact with the air. Temperature 12°, sp. gr. = 1·01219. In 10,000 parts are: KCl, 0·864; NaCl, 149·269; Na₃BO₃, 0·322; LiCl, 0·153; BaCl₂, 0·005; SrCl₂, 0·027; CaCl₂, 5·95; Ca₃(PO₄)₂, 0·014; MgCl₂, 1·304; MgBr₂, 1·132; MgI₂, 0·386; MgCO₃·CO₂, 5·044; FeCO₃·CO₂, 1·259; Al₂O₃, 0·004; Mn, trace; SiO₂, 0·226; organic C, 0·814; free CO₂, 0·756.

The amounts of iodine, bromine and chlorine are compared with those in several other springs; that of Zablacez contains the most.

L. J. S.

Physiological Chemistry.

'Survival Respiration' of Muscle. By W. M. FLETCHER (*J. Physiol.*, 1898, 23, 10—99).—The experiments were performed on frogs' muscles, and relate principally to the discharge of carbonic anhydride from these after their removal from the body. The normal course of this discharge and its modifications under various conditions, rigor, putrefaction, and action of acids and other poisons are represented in diagrams. A large series of rapidly performed estimations of carbonic anhydride was made possible by a modification of Blackman's apparatus. The first stage, extending over 5 hours, is one of irregular decline; part of the carbonic anhydride is due to destructive changes in the muscle, part to diffusion from the muscle substance,

and part to oxidation changes similar to those obtaining during life. The second stage, described as the 'plateau,' is many hours longer, and shows a very slowly declining rate of discharge; this is the stage which accompanies *rigor mortis*; it passes by gradual degrees into the third stage, in which only traces of the gas are yielded by the muscle. If putrefaction sets in, its occurrence can always be detected by a great increase in the formation of carbonic anhydride. W. D. H.

Chemistry of Contents of Alimentary Tract. By A. LOCKHART GILLESPIE (*Proc. Roy. Soc.*, 1897, 62, 4—11).—The contents of the alimentary canal in dog, calf, and probably in man, are acid throughout. When the food leaves the stomach, it rapidly becomes more concentrated from absorption of water, and consequently more acid; it still contains hydrochloric acid combined with proteid, but the increased proportion of inorganic chlorides indicates that this acid is being rapidly acted on by the soda of the pancreatic fluid. The organisms present fall into two groups, those which produce acid and those which produce alkaline substances; the former do not, as a rule, liquefy gelatin; the latter are the ordinary putrefactive organisms. The former are generally in excess; the ammonia formed by the second group unites with the lactic acid formed by the first, and the salt so formed is advantageous for the further development of both kinds. Excess of hydrochloric acid leaving the stomach causes a relatively great destruction of the alkali-forming organisms, and thus lessens decomposition in the intestine.

Salol is an antiseptic which exerts its power chiefly in the lower part of the intestine, and on the acid-forming organisms; calomel acts principally on the alkali-producing organisms, and in the upper region of the bowel.

Trypsin, although it is slowly destroyed by organic acids, is yet capable of considerable proteolytic action in their presence.

The absorption of fluids is greatest in the duodenum and lower ileum. W. D. H.

Spontaneous Emulsifying of Fatty Oils. By W. LOEWENTHAL (*Chem. Centr.*, 1897, ii, 619; from *Du Bois-Reymond's Arch.*, 1897, 258—269).—Gad (*Du Bois-Reymond's Arch.*, 1878, 181) observed that rancid oil forms an emulsion with dilute sodium carbonate solution even when the mixture is not shaken. The author finds that a 0.06 to 0.18 per cent. solution of sodium carbonate free from sodium chloride forms an emulsion most readily; with a 0.15 per cent. solution of carbonate, 6 per cent. of oleic acid must be present in the olive oil, and when 1 per cent. of sodium chloride is contained in a 0.06 per cent. solution of carbonate 2.3 per cent. of oleic acid is sufficient. The emulsifying power of the carbonate solution containing chloride is increased by adding soap solution. A content of chloride of more than 6 per cent. interferes with the action, but this effect can be compensated by adding bile; when, however, chloride is absent, or the content of acid is lower, the addition of bile hinders the formation of an emulsion. For olive or rape oil, the best conditions are attained when 9 per cent. of oleic acid in a solution of 0.06 per cent. of sodium carbonate is present; castor oil does not emulsify. E. W. W.

The Relationship of Nutrition-need to the Nitrogenous Constituents of the Body. By BERNHARD SCHÖNDORFF (*Pflüger's Archiv.*, 1898, 71, 420—426).—Pflüger found that in dogs, 1 kilo. of the body flesh demands a minimum of 2·073 grams of nitrogen in the meat given as food. On repeating these experiments, the number found (2·099) is nearly identical with Pflüger's. There are, however, circumstances in which there may be variations, but what all these circumstances are demands renewed investigation; certainly under the influence of thyroid-feeding the number is greater (2·657).

W. D. H.

Absorption and Excretion of Iron in the Human and Animal Body. By A. HOFMANN (Zurich) (*Virchow's Archiv.*, 1898, 151, 488—512).—Microchemical investigation of the wall of the alimentary canal shows that in man the principal absorption is in the duodenum. The appearances are little different when medicinal doses of iron are added to the food; the liver, and especially the spleen, are the places where iron is stored, whilst it is excreted by the kidney and large intestine. Analogous results were found in the guinea pig. It is believed that inorganic salts of iron are capable of absorption.

W. D. H.

Comparative Chemistry of the Suprarenal Capsules. By B. MOORE and SWALE VINCENT (*Proc. Roy. Soc.*, 1898, 62, 280—283).—The paired suprarenal bodies of elasmobranch fishes correspond structurally and functionally with the medulla of mammalian suprarenals. The inter-renal body corresponds to the cortex. The suprarenal of Teleostean fishes consists solely of cortex.

The chromogen obtainable from the elasmobranch paired bodies is of the same chemical nature as that found in the mammalian medulla.

W. D. H.

Phosphorus in Organic Tissues. By LÉOPOLD JOLLY (*Compt. rend.*, 1898, 126, 531—533).—Experiments have been made in order to determine whether animal and vegetable tissues contain unoxidised phosphorus in addition to metallic phosphates; the results were all negative. Among the substances examined were vegetables, and sheep's brains and flesh.

It has been found that sheep's brains contain about twice as much phosphoric acid as the muscular tissue.

J. J. S.

Influence of Acids and Alkalis on the Electrotonic Currents of Medullated Nerve. By AUGUSTUS D. WALLER (*Proc. Roy. Soc.*, 1897, 62, 80—99).—A full account of experiments previously published (compare Abstr., 1897, ii, 220).

W. D. H.

Composition of Human and Cows' Milk. By WILLIAM CAMERER and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1898, 36, 277—313. Compare Abstr., 1896, ii, 378; 1897, ii, 112).—In human milk, the material regarded by Pfeiffer as proteid contains 40 per cent. of some unknown nitrogenous substance. In 100 grams of human milk, 11 milligrams of nitrogen are contained in decomposition products like urea and ammonia; of the remaining nitrogen, 88 per cent. belongs to proteids, and 12 per cent. to unknown, probably diffusible, materials.

In cows' milk, the corresponding amounts are 18 milligrams, 98 per cent. and 2 per cent. The unknown materials of human milk are either much poorer in nitrogen than proteid, or consist of a mixture of nitrogenous and non-nitrogenous substances.

Experiments on inversion by means of dilute hydrochloric acid, with both varieties of milk, show that the carbohydrate there present, which reduces Fehling's or bismuth solution, is not increased. Pentoses were not found.

W. D. H.

Metabolism in Leucæmia and Pseudoleucæmia. By WACŁAW VON MORACZEWSKI (*Virchow's Archiv.*, 1898, 151, 22—52).—Complete tables are given of the analyses of food and excretions in a case of leucæmia and in one of pseudoleucæmia; the observations extended over a prolonged period. As a result, leucæmia is characterised as a nitrogen and phosphorus disease; pseudoleucæmia as a nitrogen disease. As in other forms of anæmia, they may be also regarded as chlorine and calcium diseases, that is to say, there is a retention in the body of the substances mentioned; the katabolic side of metabolism is in abeyance, and this is possibly connected with diminution of oxidation processes. Treatment with spleen tabloids had practically no effect; with oxygen, the excretion of phosphorus and calcium is increased; with thyroid tabloids, the metabolism becomes almost normal.

W. D. H.

Physiological Action of Hydroxylamine Hydrochloride. By W. B. BRODIE (*Proc. Roy. Soc. Edin.*, 22, 56).—Solutions of 1 per cent. strength were employed after neutralisation with acid; it appears to act as a poison to protoplasmic structures, but its mode of action is not explained; it may be dependent on some reducing action.

When the neutralised solution or a crystal of the salt which is acid is added to blood-pigment, the two dark bands of oxyhæmoglobin gradually fade and broaden out, but never absolutely disappear, whilst the part of the spectrum, from the commencement of the green to the violet, is darkened; it resembles the spectrum of alkaline hæmatin, with the addition of these two faint bands. The single band of reduced hæmoglobin is never seen.

E. W. P.

Formation of Fat during Phosphorus Poisoning. By EDUARD PFLÜGER (*Pflüger's Archiv.*, 1898, 71, 318—332).—Polimanti (this vol., ii, 307) has recently stated that in frogs, phosphorus poisoning leads to an increased formation of fat in the body. This fat is considered to originate from proteid, as the frogs employed were winter frogs in which the amount of glycogen in the body is reduced to a minimum. On this last point, Polimanti himself made no experiments, but took for granted the statements of Schiff and Luchsinger. The possibility of the origin of fat from proteid has always been strenuously resisted by Pflüger, who in the present paper subjects Polimanti's work to vigorous criticism.

He shows that frogs at the end of their winter sleep do contain a remarkably high (nearly 1.0) percentage of glycogen; he calculates that this would be more than sufficient to explain the increase of fat found in Polimanti's experiments. He, moreover, points out that

Polimanti's calculations require correction, that sufficient care was not exercised in the selection of frogs of a uniform size, and that the method of extraction of the fat was faulty. This last point is more fully discussed in a paper by Nerking (see this vol., ii, 413).

NOTE BY ABTRACTOR.—The method employed of estimating glycogen consisted in extracting the tissues with boiling potassium hydroxide; the proteid in this extract was precipitated with Brücke's reagent, and the glycogen in the filtrate precipitated with alcohol. This precipitate was weighed in some experiments, and converted into sugar in others, the number in the latter case coming out smaller than in the former; the precipitate produced by alcohol, therefore, consisted of something else in addition to glycogen, indeed the author admits it contained nitrogen. He seems altogether to have omitted a consideration of Pavy's work who has shown that proteids on treatment with potash yield an amylose carbohydrate; it appears possible that what is in the present paper called glycogen may, in part at any rate, consist of this substance.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation without Yeast Cells. V. and VI. By EDUARD BUCHNER and RUDOLF RAPP (*Ber.*, 1898, 31, 1084—1090; 1090—1094. Compare this vol., ii, 127).—Quantitative experiments with yeast extract show that the relation between the alcohol and carbonic anhydride produced by its action on sugar is practically the same as when living yeast is employed. The active enzyme is not extracted when the yeast is simply washed with water, a comparison of the extracts obtained from washed and unwashed yeast showing that when no arsenite is added, the two are equally strong, whilst in the presence of 2 per cent. of arsenious oxide that obtained from the washed yeast has a much more vigorous action.

The addition of 0.55 per cent. of ammonium fluoride causes an opalescence and greatly diminishes the activity of the extract, whilst the nitrate, chloride, sulphate, and hydrazoate of ammonium are without action. Sodium hydrazoate and toluene, both of which are strong antiseptics, have no effect on the progress of the fermentation, and it is proposed to employ 1 per cent. by volume of toluene instead of potassium arsenite. The latter appears to diminish the fermentation of glucose, galactose, and carbohydrates which yield glucose alone on hydrolysis, whilst it has no effect on saccharose and mixtures of glucose and fructose, or glucose and saccharose. It also appears to have a decided effect on dialysed or diluted extract, but no explanation of this action has as yet been arrived at.

The expressed yeast extract has an equally rapid action on maltose, saccharose, *d*-glucose, and *d*-fructose; raffinose is more slowly fermented and *d*-galactose and glycogen still more slowly, whilst lactose and *l*-arabinose are not attacked. Living yeast ferments glucose more

rapidly than fructose and does not ferment glycogen. The experiments were carried out with 13 per cent. and in some cases 28 per cent. solutions, and both in the absence of antiseptics, and in the presence of potassium arsenite and toluene.

A. H.

Production of Aromatic Substances by Alcoholic Fermentation in Presence of Certain Leaves. By GEORGES JACQUEMIN (*Compt. rend.*, 1897, 125, 114—116).—Although the leaves of most trees do not possess the characteristic odour and taste of the ripe fruit of the same tree, yet such leaves are capable of developing the odour and taste when placed in a liquid undergoing alcoholic fermentation. Apple, pear, and vine leaves have been treated in this manner. The author suggests that the aromatic principle is probably present in the leaves in the form of a glucoside, and that the glucoside is hydrolysed in the one case by an enzyme secreted by the yeast and in the other by an enzyme contained in the ripening fruit.

J. J. S.

Oxydase from Botrytis Cinerea. By J. B. VINCENT LABORDE (*Compt. rend.*, 1898, 126, 536—538).—As has been previously shown, *Botrytis cinerea*, which lives as a parasite on grapes, secretes an oxydase which is afterwards found in the must, and also after fermentation in the wine. This oxydase is the cause of the alteration known as “casse brune.”

A method of estimating oxydase has been employed which depends on a comparison of the depth of the blue coloration which it yields with guaiacum extract, with the colour produced between iodine and the same extract (0.5 milligram of iodine to 20 c.c. of mixture gives a colour which is taken as unity).

Oxydase is gradually destroyed by atmospheric oxygen and also by heat, the destruction being complete at 85°.

The author finds that the quantity of oxydase left at the end of a fermentation is always less than the quantity originally present, and that the amount left decreases with the length of time taken for the fermentation. The difference in temperature, 25—36°, does not affect the amount. Injurious yeasts and organisms do not appear to affect oxydase. In the case of red wines, the amount of oxydase left is always much greater than in the case of white wines, and may amount to 80—100 per cent. of the amount originally present.

J. J. S.

Action of “Flower of Wine” on Sorbitol. By GABRIEL BERTRAND (*Compt. rend.*, 1898, 126, 653—656).—The author has repeated and extended his previous experiments and again finds that, contrary to the statement of Matrot, the “flower of wine” (*Saccharomyces vini*), when growing in a nutritive liquid containing sorbitol, gradually destroys the latter and does not convert it into sorbose. This holds good in a variety of conditions and for various juices containing sorbitol.

C. H. B.

Saké, the Japanese National Beverage, and the Fungus which produces it. By OTTOKAR SHIEWECK (*Bied. Centr.*, 1898, 27, 140—141; from *Centr. Bakt. Par.*, 1, ii, 782).—The liquid is prepared

by fermenting steamed rice with "koji," which is obtained by mixing rice grains which have been freed from husks, soaked and steamed, with 0.2 per cent. of Tam koji seeds, which are already infected with *Aspergillus oryzae*. The whole process, which is rather complicated, is described. The final product of the fermentation is pressed in cotton bags, the saké drawn off into tubs, and allowed to ferment further; the pressed residues yield alcohol and are afterwards utilised as manure. Saké, which contains up to 15 per cent. of alcohol, is consumed hot, has the colour of hock, and in taste resembles old Hungarian wine.

It is supposed that the fermentation is caused by special yeasts, in part true yeasts (*Saccharomyces anomalus* and a yeast with round spores), which are mixed with *Aspergillus*. Experiments with different substances showed that *Aspergillus* developed best on rice and worst on apple sections. N. H. J. M.

Fungi which Thrive in Acids. By CARL WEHMER (*Bied. Centr.*, 1898, 27, 284—285; from *Beitr. Kennt. einheim. Pilze*, 2, Jena, 1895).—The flakes produced in pure solutions of citric acid are sterile mycelia, which, when transferred to suitable nutritive solutions, eventually fructify and prove to be *Verticillium glaucum*. No other fungi seem to develop in pure citric acid solutions, but when sugar is added, spores of other kinds are readily detected.

In pure tartaric acid solutions, a mould develops which is capable of existing in presence of extraordinarily large amounts of acid. A growth which had developed in a 13.3 per cent. solution was found to produce vigorous citric acid fermentation in sugar solutions. The same fungus, together with *Penicillium luteum*, appeared on lemons, and both fungi are soon observed in saccharine solutions to which citric or tartaric acids have been added. N. H. J. M.

Nutritive Value of Sodium Salts for Fungi. By CARL WEHMER (*Bied. Centr.*, 1898, 27, 285; from *Beitr. Kennt. einheim. Pilze*, 2, Jena, 1895).—The statement that, in nutritive solutions for fungi, potassium salts may be replaced [?] by sodium salts] is based on a few old, and admittedly imperfect, experiments. It is now shown that *Aspergillus* and *Penicillium* may develop considerably in nutritive solutions containing, besides a non-nitrogenous organic substance and magnesium sulphate, only sodium phosphate and sodium nitrate. The growth was, however, much slower than in similar solutions containing potassium salts. Sodium salts are, therefore, not worthless as foods, but only less suitable than potassium salts. N. H. J. M.

Physiological Inequality of Fumaric and Maleic Acids: Antiseptic Action of Maleic Acid. By CARL WEHMER (*Bied. Centr.*, 1898, 285; from *Beitr. Kennt. einheim. Pilze*, 2, Jena, 1895).—Buchner's experiments (*Abstr.*, 1892, 820) with the ammonium salts of fumaric and maleic acids showed that fungi developed with great difficulty in the maleate solution, and this was supposed to indicate that maleic acid is not available as a source of carbon. In the author's experiments, both the free acids and salts were employed. The results show that maleic acid is directly injurious, and that as an

antiseptic for mould fungi it is nearly equal to hydrochloric and oxalic acids, whilst its action on bacteria is similar to that of salicylic acid (compare Ishizuka, Abstr., 1897, ii, 276). N. H. J. M.

Physiology and Morphology of the Acetic Acid Bacteria. By W. SEIFERT (*Bied. Centr.*, 1898, 27, 123—130; from *Centr. Bakt. Par.*, 1897, 3, 337—349 and 385—399).—Methylic and isopropylic alcohols are not attacked by *Bacterium Pasteurianum* and *B. Kützianum*. Amylic alcohol is not attacked by *B. Past.*, but the results with *B. Kütz.* were uncertain. Ethylic and propylic alcohols are converted by both bacteria into acetic and propionic acids respectively, and butylic and isobutylic alcohols are also oxidised. Ethylenic glycol is oxidised to glycolic acid, which, however, checks the development of the bacterium. Both bacteria act very feebly on glycerol as compared with *B. aceti Brown*. Mannitol is not attacked at all by *B. Past.*; *B. Kütz.* converts it into levulose with only slight energy as compared with *B. aceti Hansen* and *B. aceti Brown*. Neither bacterium acts on dulcitol or on levulose or maltose. Dextrose is oxidised by both bacteria to gluconic acid (which retards the activity of the bacteria), and acetic acid to carbonic anhydride and water; propionic and butyric acids, however, do not seem to be attacked.

The effect of the acetic acid bacteria on monatomic primary alcohols seems to diminish as the amount of carbon increases. N. H. J. M.

Action of Light on Diastase, and its Biological Significance. By J. REYNOLDS GREEN (*Proc. Roy. Soc.*, 1897, 61, 25—28. Compare Abstr., 1896, i, 110).—Brown and Morris have pointed out (*Trans.*, 1893, 604) that the amount of diastase in foliage leaves is greater in the early morning than in the latter part of the day, especially after several hours of sunshine; the author now describes experiments which were made to ascertain whether the diminution in quantity during the day is due to the destructive influence of light on the enzyme. The diastatic solutions employed were extract of malt; aqueous solutions of diastase precipitated by alcohol from malt extract; diluted human saliva, freed from mucin; and extracts of foliage leaves. These were preserved by the addition of 0.2 per cent. of potassium cyanide, and, in the author's experiments, were exposed to the action of light during several hours, either to the whole of the spectrum or to a selected part of it. Their hydrolytic power was then determined by digesting them with dilute solutions of soluble starch, or 1 per cent. starch paste, titrating against Fehling's solution, and weighing as cupric oxide the precipitate thus obtained. Control experiments were made in each case, so that any difference in hydrolytic power was attributable solely to the illumination. The sources of the latter were bright sunshine, diffused daylight, and a powerful, naked electric arc.

The results obtained may be summarised as follows. Exposure to the whole of the spectrum during several hours destroys from 20—60 per cent. of the diastase, whilst an increase in the amount of the latter occurs at first, when the ultra-violet rays are cut off; subsequently, however, the enzyme is gradually and completely destroyed. The infra-red, red (720 $\mu\mu$ to 640 $\mu\mu$), orange (640 $\mu\mu$ to 585 $\mu\mu$), and

blue (500 to 430 $\mu\mu$) regions gave increases in the amount of diastase of 10.8, 53.5, 4.75 and 20.8 per cent. respectively; the green region from 585 $\mu\mu$ to 500 $\mu\mu$, however, caused a diminution of 15.7 per cent., and a marked decrease was found in the violet region beyond 430 $\mu\mu$, although this was not measured. It is noteworthy that the increase or decrease of diastase in the several cases continued after the solutions were removed from the access of the rays. The deleterious rays were found to be absorbed by the solutions, partly by the diastase, whether boiled or unboiled, and partly by the proteids present. The latter seem to exercise a protective influence; this was determined separately, by adding small quantities of egg-albumin to the extracts, and appears to be roughly proportional to the amount of albumin present. The colouring matter of barley also acts as a protection.

The author finds also that diastase is destroyed by light in the living leaf, as well as in the extracts, but was unable to determine the probable protective influence of the chlorophyll in the leaf.

The following conclusions are drawn from the experiments. (1) That there exists in the leaf, and in the extracts examined, a certain amount of zymogen, which is converted by the infra-red, red, orange, and blue rays into active diastase. (2) That diastase is destroyed by the ultra-violet and violet rays, or its configuration is so changed that it is unable to effect starch hydrolysis. (3) The enzyme is not located in the chlorophyll grains, but in the protoplasm of the cell. (4) The suggestion of Pick (*Bot. Centr.*, 16, 9—12), and of Johow (*Pringsheim's Jahrb.*, 15, 299), that the red colouring of certain leaves is a material help to the translocation of starch, is probably sound, as such colouring matters absorb the rays which destroy the diastase. (5) That the power of utilising the radiant energy of light is possessed by many plants, without the presence of a chlorophyll apparatus.

W. A. D.

Alcohol Production during the Intramolecular Respiration of Higher Plants. By EMIL GODLEWSKI and F. POLZENIUSZ (*Bied. Centr.*, 1898, 27, 135; from *Anzeiger Akad. Wiss. Krakau*, 1897).—Ten pea seeds kept in a vacuum, with water, yielded daily 10—20 c.c. of carbonic anhydride for three weeks. The total amount of carbonic anhydride obtained in six weeks, when there was no further evolution, amounted to 20 per cent. of the dry substance of the seeds. An amount of alcohol was simultaneously produced corresponding very well with the quantity which would be obtained by ordinary fermentation. When 2 per cent. glucose was used instead of water, there was an increased production of alcohol and carbonic anhydride owing to the partial decomposition of the glucose. Cane-sugar was inverted by the seeds in absence of air.

When kept in water (without air) for 14 days, peas still retain the power of germinating, but germination is not normal, and the roots die before the plumula.

It is concluded that the action of yeast differs only quantitatively from that of the intramolecular respiration of plants.

N. H. J. M.

Anatomy and Physiology of the Seed of Sugar Beet (*Beta vulgaris*). By ANTON NESTLER and JULIUS STOKLASA (*Bied. Centr.*, 1898, 27, 115—117; from *Neue Zeit. Rübenzuckerind.*, 1897, 39, 37).—Nearly the whole of the lime of the seed is contained in the testa, which contains numerous crystals of calcium oxalate. The testa also contains a large amount of pentosans (18·85 per cent. in the dry matter) probably (especially the xylan) chemically combined with much of the cellulose. The seed, excluding the outer testa, contains the following amounts of the different constituents.

Total nitrogen.	Proteid nitrogen.	Fat (without lecithin).	Lecithin.	Cellulose.	Pentosans.	Starch.	Ash.
4·32	3·85	20·02	0·46	2·31	2·26	37·31	3·52

The ash contains (per cent.).

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .
20·14	8·00	3·83	11·20	0·47	43·22	9·02	2·81

The proteids are mainly in the embryo, and sometimes amount to 24 per cent. The fat plays a very important part during germination, and is at this time almost entirely consumed. Lecithin occurs almost exclusively in the embryo and starch mostly in the perisperm. The hemicellulose in the cotyledons presumably contain pentosans (araban) as well as galactose (compare Schulze, *Zeit. physiol. Chem.*, 1896, 392).

The ash constituents (especially phosphoric acid, sulphur, iron, and magnesium) seem to be mostly in combination with organic substances; the potash is supposed to be accumulated in the perisperm, along with the carbohydrates.

N. H. J. M.

Cause of the Presence of Oxalic Acid in Sugar-juices. By G. VON KRIES (*Chem. Centr.*, 1897, ii, 921; from *Zeit. Ver. Rübenzuck.-Ind.*, 1897, 755—757).—In connection with Rümpler's observation (*Deutsch. Zuck.-Ind.*, 1897, 678), that sugar solutions which contain at least 1 per cent. of calcium oxide are able to dissolve calcium oxalate at the ordinary temperature, the author finds that the presence of alkali carbonates enables the juices to hold oxalic acid in solution or to extract it from the sediment.

E. W. W.

Substances contained in the Trunks of Trees. By FRANCIS H. STORER (*Chem. Centr.*, 1897, ii, 902—903; from *Bulletin of the Bussey Institution*, 2, 386, 408).—The author finds that the quantity of starch stored in the trunks of trees is not so great as is usually assumed and that pentosans are to be regarded as the reserve material. The following data in parts per 100 of wood dried at 100° were obtained in the case of white birch (*Betula populifolia*).

	Inner wood.		Outer wood.		Bark.	
	Pentosan.	Starch.	Pentosan.	Starch.	Pentosan.	Starch.
In May	39·23	4·93	36·10	5·42	30·82	7·67
In July	30·52	3·83	34·67	3·87	21·07	7·52
In October...	29·83	3·75	29·97	3·51	22·67	4·24

The amount of pentosan was estimated by distilling the wood with hydrochloric acid of sp. gr. = 1.06 and weighing the furfuraldehyde in the form of its phenylhydrazine compound; when 2.5 per cent. or a still more dilute acid was used, and the sugar estimated by Allihn's method, the more dilute the acid the less the amount of pentosan obtained and the residue when distilled with acid of sp. gr. = 1.06 gave abundance of furfuraldehyde. The starch was estimated from the amount of sugar obtained by the action of diastase. The content of wood-gum determined by Loew's method was found to be 13—14 per cent. in the wood and 6.8 per cent. in the bark, and the crude fibre by Weende's method 52.5—55.2 in the wood. This crude fibre also contains pentosan and yields furfuraldehyde when distilled with hydrochloric acid. Lange's method gave similar results and the cellulose was also found to contain pentosan.

E. W. W.

Feeding Experiments on Milch Cows with Linseed Oil and Crushed Linseed. By D. MELIK. BEGLARIAN (*Bied. Centr.*, 1898, 27, 239—240; from *Milchzeit.*, 1897, 552).—Four cows were fed during four periods of 8 days as follows. Period (1 and 4), beetroot, 50 kilos.; hay, 14 kilos.; straw, 3 kilos.; malt germs, 4 kilos.; linseed meal, freed from oil, 4 kilos.; and barley meal, 2 kilos. per 1000 kilos. live weight. Period (2), the same as (1 and 4), with linseed oil (1 kilo.), as an emulsion, in addition. In period (3) the feeding was the same as in (1 and 4), except that crushed linseed (4 kilos.) was substituted for linseed meal.

The emulsified oil caused loss of appetite, but the crushed linseed was eaten readily. As regards the effect of the oil, or oily food, on the production of fat, the results were, unlike Soxhlet's, entirely negative.

It is considered that further experiments are desirable. (Compare Soxhlet, *Wochenbl. landw., Ver. Bayern*, 1896, and *Journ. R.A.S.E.*, 1897, [iii], 8, 655; also Speir, *Trans. Highland and Agric. Soc. Scotl.*, 1897, [v], 9).

N. H. J. M.

Manuring Experiments with Potash and Soda. By SMETS and C. SCHREIBER (*Bied. Centr.*, 1898, 27, 227—229; from *Recherches sur les engrais potassiques et sodiques*, *Maaseyck.*, 1896).—The exclusive application of sodium salts to soil very poor in available potash has little or no effect on the vegetation, but has a distinct effect in the case of soils containing a moderate amount of potash. With poor soils, sodium salts should be applied along with potassium salts. In presence of much potash, soda is without effect. Soda is useful in economising potash, but is not necessary to vegetation.

Experiments with oats on different soils showed that the soda in kainite and carnallite has an effect between 5 and 80 per cent. of the effect produced by the potash. Other experiments, with different crops, indicated an effect produced of 6 to 36 per cent. of that shown by the potash.

N. H. J. M.

Analytical Chemistry.

Estimation of Perchlorate in Saltpetre. By R. SELCKMANN (*Zeit. angew. Chem.*, 1898, 101—102).—Five or 10 grams of the sample of Chili-saltpetre which has been assayed for chlorides is fused in a porcelain crucible of 40—50 c.c. capacity with 3—4 times its weight of lead-cuttings. Soon after the nitrate fuses, the lead begins to melt, and evolution of oxygen and formation of litharge is noticed. To promote the action, the mass is well stirred with a bent copper wire, and when, after about 15 minutes, the mixture has become pasty, the heat is raised for a few minutes to dull redness. When cold, the melt is warmed with water containing a few grams of sodium hydrogen carbonate or hydroxide, and the filtrate containing the chlorine is acidified with nitric acid, precipitated with silver nitrate, and the silver chloride collected and weighed.

When dealing with ordinary saltpetre, the heating should be conducted cautiously at first, and finally somewhat more strongly for half an hour, to completely decompose the perchlorate. The test-analyses are satisfactory.

L. DE K.

Detection of Iodine in Organic Preparations. By ANTON SEYDA (*Chem. Centr.*, 1897, ii, 806—807; from *Zeit. öffentl. Chem.*, 3, 359—364).—*In Cod-liver Oil.*—Twenty grams of the sample is thoroughly mixed with 40 grams of powdered sodium hydroxide contained in a nickel dish of 200 c.c. capacity, and then heated over a burner. After the first frothing is over, the dish is covered with a platinum lid and the heat is continued for 8 hours, the mass being from time to time stirred with a clean iron spatula. The residue is then transferred to a beaker and dissolved in 400 c.c. of water, and after removing the carbonaceous residue by filtration, a current of carbonic anhydride is passed into the filtrate until the alkali is completely neutralised, which may be ascertained by the well-known barium chloride test. When cold, an equal volume of commercial absolute alcohol is added to precipitate the sodium carbonate, which is collected, and washed thrice with proof spirit. The mixed alcoholic liquid is then concentrated on the water bath, transferred to a platinum dish, and again carefully evaporated to dryness, and gently ignited until it becomes white. When cold, it is dissolved in a little water, and mixed in a separating funnel with 5 c.c. of a 0.01 per cent. solution of potassium nitrite, 10 c.c. of chloroform is added, and the whole well shaken; the liquid is then acidified with dilute sulphuric acid, and again thoroughly shaken. When the two layers have completely separated, the chloroform is drawn off and filtered into a glass cylinder of 10 cm. diameter through a dry filter. The presence of iodine is indicated by the characteristic purple coloration of the chloroform, which is rendered more visible by comparing it with a similar cylinder containing pure chloroform.

In Oophorin.—This pharmaceutical preparation is prepared from

pigs' ovaries. Twenty grams of the sample is treated as directed for cod-liver oil. A sample analysed by the author showed, however, no trace of iodine.

L. DE K.

Test for Sulphurous Acid : Estimation of Iron with Dichromate. By H. JERVIS (*Chem. News*, 1898, 77, 133).—In reducing ferric solutions with sulphurous anhydride, the complete expulsion of the excess of the gas is best ascertained by testing the vapour from the boiling liquid with a few drops of a very dilute acid solution of permanganate.

It has been suggested that traces of iron may be estimated in ignited manganese oxide by dissolving in hydrochloric acid, reducing, and titrating with dichromate. This is not correct, as in presence of much manganous salt the blue colour of the ferrous ferricyanide is not seen, being masked by the brown manganous ferricyanide.

D. A. L.

Valuation of Fuming Sulphuric Acid and of Sulphuric Anhydride.—By R. ROSENLECHER (*Zeit. anal. Chem.*, 1898, 37, 201—217).—The following method was devised for the rapid assay, for technical purposes, of numerous samples of the above substances, by operators not accustomed to refined analytical work. From a glass tube 5—6 mm. in diameter, light bulbs, each with two narrow tubes, are drawn out; while expanding each bulb, its tubes are bent out from a straight line to an angle of about 140° , and their ends are then reduced in bore to $\frac{1}{4}$ to $\frac{1}{2}$ mm. It is convenient to have one tube 4—5 c.m., the other 5—6 c.m., in length. Plunging the longer tube into the sample of acid (previously, if necessary, completely liquefied, by suitable, but not excessive, warming in a stoppered bottle), it is easy by suction to draw some of the acid into the bulb without any of the white anhydride fumes passing beyond it. The bulbs can be hung from the balance in an appropriate wire stirrup, and owing to the narrowness of the tubes neither loss of anhydride nor absorption of water is to be feared during the weighing. Warming the bulb by the hand is naturally to be avoided. Each bulb is then thrust into a bottle (250—300 c.c.) containing 20—30 c.c. of distilled water and 10 drops of an indicator (paranitrophenol is preferred) and held horizontally. It is easy to insert the stopper and seal it by wetting with the water inside before any escape of acid occurs. A sudden shake then pulverises the bulb, and the white fumes which fill the bottle are allowed to disappear by absorption before the stopper is removed. The titration with alkali is then completed in the same bottle. Duplicate assays seldom differ by more than a few hundredths per cent.

M. J. S.

Iodometric Estimation of Tellurium. By JAMES F. NORRIS and HENRY FAY (*Amer. Chem. J.*, 1898, 20, 278—283).—The following method affords an accurate means for the estimation of tellurium in presence of the halogen acids.

Tellurous acid is oxidised to telluric acid by adding potassium permanganate until the meniscus of the brown solution shows a deep pink colour. The whole is then diluted with ice-cold water, treated with potassium iodide and sulphuric acid, and titrated

with sodium thiosulphate. The oxidation of tellurium may be expressed by the following equation, $2\text{KMnO}_4 + 3\text{TeO}_2 + 4\text{KI} + 5\text{H}_2\text{SO}_4 = 3\text{TeO}_3 + 3\text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{H}_2\text{O} + 4\text{I}$.

The authors find that pure, perfectly white, tellurium dioxide may be obtained by decomposing the basic nitrate just below a red heat and then fusing quickly in small portions. If the nitrate be fused directly, traces of tellurium always separate. A. W. C.

Method for Estimating Free Acid in the Presence of Phosphates. By L. DE JAGER (*Chem. Centr.*, 1897, ii, 683—684; from *Centr. med. Wis.*, 1897, 593—596).—The process is very much like the well-known method proposed by Leo; it is carried out by titrating the boiling solution with N/10 soda, using phenolphthalein as indicator, the liquid turning red the moment all the lime has been precipitated as tricalcium phosphate. If no lime is present, another estimation must be made after adding some calcium chloride.

If free lime is present, this is quantitatively removed by oxalic acid, and another titration is made. Formulæ are given to facilitate the calculation. L. DE K.

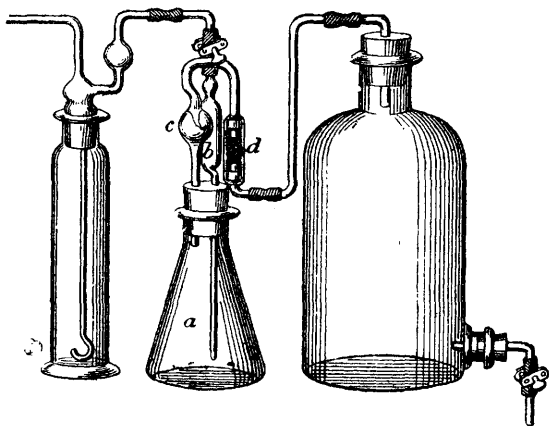
A Gravimetric Method of Estimating Phosphoric Acid as Ammonium Phosphomolybdate. By THOMAS S. GLADDING (*Chem. News*, 1898, 77, 32—33. Compare *Abstr.*, 1896, ii, 336).—The author obtains a uniform molybdate precipitate in the following manner, and approves of its use for the estimation of phosphoric acid. Twenty-five to 50 c.c. of the phosphoric solution is treated with 25 c.c. of ammonia, of sp. gr. 0.900, then acidified with nitric acid, of sp. gr. 1.420, and placed on a water bath maintained at 50°, while the ordinary 5 per cent. acid molybdate solution is dropped in with constant stirring, at the rate of 50 c.c. in 5 minutes, until there is an excess of 10 c.c.; after a further 10 minutes on the water bath, the mass is filtered through a weighed filter. The filtrate is mixed with 5 c.c. of molybdate solution, and should remain clear or become only slightly opalescent after being on the water bath 10 minutes. The precipitate is washed with dilute nitric acid (100.1), three times by decantation, and three times on the filter, and finally once with water; it is then drained, dried first in an ordinary water oven, and finally at 105°, in an oven surrounded with dilute glycerol, sp. gr. = 1.160, and boiling at 110°. The filter paper must be tared to that temperature. The various precautions ensure the absence of occluded salts, the complete precipitation of the phosphoric acid, and the non-separation of molybdic oxide or iron salt. The author finds the composition of the yellow crystallised salt to be: $24\text{MoO}_3, \text{P}_2\text{O}_5, 3(\text{NH}_4)_2\text{O} + 24\text{MoO}_3, \text{P}_2\text{O}_5, 2(\text{NH}_4)_2\text{O}, \text{H}_2\text{O} + 5\text{aq}$.

For the direct estimation of reverted or citrate-soluble phosphoric acid, the citrate filtrate and washings are made up to 200 c.c. and 25 c.c., equivalent to 0.25 gram of the fertiliser, is treated with 50 c.c. of ammonia, of sp. gr. 0.900, acidified with nitric acid, made up to half a litre, heated in a bath to 65°, while 50 c.c. of molybdate solution is added in a thin stream with stirring, the whole digested for half an hour, and then treated as above, except that the filtrate is heated for half an hour at 65°, when it should remain clear. D. A. L.

Volumetric Estimation of Phosphoric Acid. By AUGUST HEBBRAND (*Zeit. anal. Chem.*, 1898, 37, 217—223).—The method advocated is essentially that of Stolba (*Abstr.*, 1877, ii, 355), and possesses the advantage over the gravimetric estimation as magnesium pyrophosphate, that it gives identical results with monammonium magnesium phosphate, and with diammonium magnesium phosphate, $(\text{NH}_4)_2\text{MgP}_2\text{O}_7$, the admixture of the latter with the precipitate of the former having been recognised by Neubauer as the chief source of error in the gravimetric method. The precipitate obtained in the usual manner is collected in an ordinary filter, and after washing sufficiently with 2·5 per cent. ammonia, the ammonia is displaced by washing with about 30 c.c. of 96 per cent. alcohol. The still moist precipitate is then rinsed back into the precipitation beaker and treated with a small measured excess of N/5 hydrochloric acid, in which it readily dissolves. About 5—10 drops of an alcoholic solution of Merck's carminic acid (0·5 gram in 100 c.c.) is added as an indicator, and the excess of acid is titrated back with N/5 sodium hydroxide. The change of colour from yellowish-brown to violet occurs when one atom of the hydrogen of the phosphoric acid has been replaced by metal, so that the factor 0·0071, multiplied by the number of c.c. of N/5 acid consumed, gives the weight of P_2O_5 in grams. Some practice is required to recognise the point at which the colour changes, and an indicator acting more sharply would be an improvement, but the results quoted leave little to be desired on the score of accuracy.

M. J. S.

Apparatus for the Estimation of Carbonic Anhydride. By GEORG F. KUNTZE (*Chem. Centr.*, 1897, ii, 637—638; from *Pharm. Centr. H.*, 38, 509—511).—The apparatus consists of an Erlenmeyer flask, *a*, which contains the substance to be tested, and serves as a



generating flask. It is made in such a way that it stands perfectly steady on the balance. The pipette, *b*, which holds the acid, is bent sideways, and provided with an elongated bulb to prevent accidents;

when filling, it is closed by means of an india-rubber tube fitted with a screw clamp. The drawn-out part does not dip into the liquid in the flask. A duplex condenser, *c*, resembling a Peligot bulb tube, with an S-shaped tube at its end, serves to carry off the evolved carbonic acid. This arrangement prevents any undue excess of moisture from getting into the calcium chloride tube, *d*, as it nearly all condenses in the bulb or the S-tube.

The calcium chloride tube is fitted with a rectangularly bent and drawn out delivery tube, which is fitted with india-rubber caps when the apparatus is weighed. To make an analysis, 0.5—1 gram of the sample is introduced into the flask and mixed with 2 c.c. of water, care being taken not to get any of the substance on the sides of the flask. The pipette is filled with acid, closed, and put through the india-rubber cork, and the whole weighed; the acid is then allowed to drop on to the carbonate, and the dissolved carbonic anhydride is expelled by warming the flask on an asbestos plate, the last traces being removed by means of the aspirator.

L. DE K.

Estimation of Added Alkali in Beer. By EDUARD SPAETH (*Zeit. angew. Chem.*, 1898, 4—5).—The author recommends the following method for the estimation of added sodium carbonate in beer: 500 c.c. of the sample freed from carbonic anhydride is mixed with 100 c.c. of ammonia, and after the earthy phosphates have completely separated, the liquid is filtered, and 60 c.c. of the filtrate (= 50 c.c. of sample) is incinerated, and the phosphoric acid estimated by the molybdate method. Another 250 c.c. of the filtrate is mixed with 25 c.c. of basic lead acetate, allowed to settle, and 200 c.c. of the filtrate is evaporated to a small bulk, and then made up again to 200 c.c. After adding a few drops of acetic acid, the excess of lead is precipitated with hydrogen sulphide, and the whole filtered; 150 c.c. of the liquid is evaporated to dryness, the residue incinerated, and the alkali in it estimated with decinormal acid. The amount of phosphoric anhydride, multiplied by 1.4, equals the amount of acid necessary for the neutralisation of the normal alkalinity of the sample.

L. DE K.

Ammonia-Soda. Analysis of Refuse Liquid. By KONRAD W. JURISCH (*Zeit. angew. Chem.*, 1898, 273—274).—After obtaining a thoroughly representative sample, the following scheme of analysis is recommended. *A*. Twenty-five c.c. of the sample is titrated with normal hydrochloric acid, using litmus as indicator; to completely dissolve the calcium carbonate, warming must be resorted to, if necessary. The result represents the total calcium hydroxide, calcium carbonate, and ammonia. *B*. One hundred c.c. of the sample is mixed with 35 grams of ammonium chloride dissolved in water, and the whole is, after a while, diluted to 1 litre. Five hundred c.c. is then filtered off and titrated with normal acid; this will represent the calcium hydroxide and the ammonia. *C*. Another 100 c.c. of the filtrate *B* is mixed with excess of ammonium carbonate, and then boiled until no more ammonia escapes. The precipitate is collected and titrated with the acid; this represents the calcium hydroxide and any calcium chloride. *D*. One hundred c.c. of the sample is distilled with calcium hydroxide, and the ammonia in the distillate is titrated.

E. Ten c.c. of the sample is diluted to 100 c.c., and of this 10 c.c. is taken and titrated with N/10 silver nitrate to get the amount of chlorine, potassium chromate serving as indicator; any chlorine not in combination with calcium is calculated to sodium chloride. The calculation will be easily understood. Convenient formulæ are given.

L. DE K.

Analysis of Calcium Carbide. By HEINRICH BAMBERGER (*Zeit. angew. Chem.*, 1896, 196—198; 243).—The process is the same as that generally used for estimating carbonic anhydride by the loss in weight. A rather large carbonic acid apparatus, fitted with calcium chloride tube, is charged with 200 c.c. of brine, and this is allowed to drop slowly on to 50 grams of the coarsely-powdered sample. The loss in weight after the action is over represents the acetylene given off.

The apparatus may be connected with the 10-bulb tube devised by Lunge, containing hypochlorite (this vol., ii, 55), and any hydrogen phosphide thus estimated. If it is desired to estimate the volume of the evolved acetylene, this may be conveniently done by allowing brine to act on a weighed quantity of the sample, and collecting the gas in a gasometer filled with brine saturated with acetylene, which is allowed to run out from the bottom into another similar reservoir. When the action is over, the liquid in the two reservoirs is brought to the same level, and the volume of the gas is read off.

L. DE K.

Estimation of Lead and Antimony in Tin-foil. By ANTON SEYDA (*Chem. Centr.*, 1897, ii, 810—811; from *Zeit. für öffentl. Chem.*, 3, 364—371).—*Estimation of Lead.*—Ten grams of the foil is dissolved in about the calculated amount of warm 25 per cent. hydrochloric acid. If more than 1 per cent. of antimony is present, this will be for the most part left undissolved; about the calculated amount of 25 per cent. nitric acid is now added, which dissolves the antimony and peroxidises the tin. The liquid is then slowly poured into a little more than the calculated quantity of hot 25 per cent. aqueous soda, which should cause an almost clear solution to form; after adding a little precipitated sulphur, hydrogen sulphide is passed in until the liquid becomes of a clear yellow. After 24 hours, the black precipitate of lead sulphide is thoroughly washed with hot yellow sodium sulphide, and then converted into lead sulphate by the action of nitric and sulphuric acids.

Separation and Estimation of Antimony.—One hundred c.c. of fuming nitric acid is put into a flask, and a small portion of 5 grams of the foil is introduced; 25 c.c. of water is added to start the action, and then gradually the remainder of the tin. The oxides thus formed are transferred to a porcelain dish, the flask rinsed with 25 per cent. nitric acid, and after evaporating to dryness, and drying for some time at 100°, the oxides are gradually introduced into 60 grams of sodium hydroxide, previously heated to fusion. This causes the formation of sodium stannate and antimonate, which are separated in the usual way by means of weak alcohol; the insoluble antimony compound should be again fused with 10 grams of sodium hydroxide. The antimony sulphide obtained later on from the sodium compound

may contain lead, copper, iron, nickel, &c., and should be digested with sodium sulphide solution. On adding acid, the antimony sulphide should be precipitated with its characteristic orange colour.

L. DE K.

Analysis of Aluminium. By FR. SIBBERS (*Chem. Centr.*, 1897, ii, 808—810; from *Pharm. Zeit.*, 42, 622).—The author states that, when dissolving aluminium in hydrochloric acid, as much as 0.3 per cent. of the silicon may volatilise as hydrogen silicide; this silicon may, however, be to some extent recovered by dissolving the metal in a small flask, from which the air has been previously expelled by a current of hydrogen free from silicon. The delivery tube consists of two parts, a calcium chloride tube, and a weighed tube, bent rectangularly downwards and not drawn out to a point. On igniting the hydrogen, the silicon burns to silica, which is deposited on the outer side of the tube.

L. DE K.

Separations from Chromic Acid: I. Separation of Iron; II. Separation of Manganese. By HARRY BREARLEY (*Chem. News*, 1898, 77, 49—50, 131—133. Compare this vol., ii, 143).—*Separation of Iron.*—On boiling from 50 to 120 c.c. of a solution of potassium chromate containing $12\frac{1}{2}$ grams per litre with 1 gram of iron as ferric chloride, a precipitate forms which cannot be filtered, but settles completely after some days; an examination of the supernatant liquor shows, however, that the separation of the iron and chromium is imperfect; moreover, the precipitate gradually re-dissolves in the cold, first becoming less and less basic; later the iron and chromium dissolve proportionately. When a gram of iron as an acid solution of ferric chloride was precipitated hot with an equivalent amount of sodium carbonate, the chromate added, and the solution made up to a litre and boiled, the liquor separated by fractional precipitation showed chromium increasing with the amount of chromate added, but even with 100 c.c. the separation was imperfect. With 1 gram of iron and 30 c.c. of chromate solution, the whole being made up to a litre, complete separation could be obtained by the use of 2N alkali in excess, that is, more than 50 of ammonia, 50 of sodium carbonate, or 30 of sodium hydroxide.

Separation of Manganese.—Half a gram of manganese as manganous chloride, along with 50 c.c. of the chromate solution, acidified and diluted to half a litre, was used in these experiments. With sodium hydroxide, the recovery of chromium increased with the quantity of alkali, but was worse in hot than in cold solutions; in all cases, the manganous hydroxide absorbed oxygen from the air, although this was less marked in hot solutions. With bromine and ammonia, the separation improves with the quantity used, in fact, an approximately accurate separation can be effected by using large quantities of these reagents. With 10 c.c. of 2N sodium carbonate, the chromium recovery was complete from solutions treated in the cold and filtered without heating, and nearly so from cold solutions heated to boiling before filtration, but far from perfect from boiling solutions in which, too, contrary to the behaviour of any other precipitant, an increased excess gave a decreased recovery. With sodium phosphate, the separation

of manganese and chromium is complete when an excess of 50 per cent. of disodium phosphate is used, 20 c.c. or more of normal ammonia added, the precipitate allowed to settle, and the solution syphoned and filtered off, if chromium alone is sought; or the phosphate precipitate may be re-dissolved in hydrochloric or sulphuric acid, the ammonia added, and the precipitate left to crystallise if the manganese is also to be estimated.

D. A. L.

[Detection and Estimation of Thorium.] By GREGOIRE N. WYROUBOFF and AUGUSTE VERNEUIL (*Compt. rend.*, 1898, 126, 340—343).—See this vol., ii, 339.

A Method of Estimating Acetylene applicable to Hydrocarbons of the type $RC\equiv CH$. By R. CHAVASTELON (*Compt. rend.*, 1896, 125, 245—246. Compare *Abstr.*, 1897, i, 545).—Acetylene reacts with an excess of silver nitrate in either aqueous or alcoholic solution according to the equation $C_2H_2 + 3AgNO_3 = C_2Ag_2, AgNO_3 + 2HNO_3$.

The author suggests this as a basis for estimating the amount of acetylene in gaseous mixtures, namely, by titrating the amount of nitric acid liberated. The gas must be free from acid vapours, and the operation is best carried out in a Raoult absorption eudiometer. The method is a general one for hydrocarbons of the type $RC\equiv CH$.

J. J. S.

Analysis of Acetylene. By WALTHER HEMPEL and LEOPOLD KAHL (*Zeit. angew. Chem.*, 1898, 53—55).—The most dangerous impurity in acetylene is hydrogen phosphide, to estimate which the authors, after many trials, now recommend the following process. The gas is measured over mercury and then transferred to a gas pipette partially filled with mercury, and containing 3 c.c. of a solution of copper sulphate, made by dissolving 15.6 grams of crystallised copper sulphate in 100 c.c. of water, and adding 5 c.c. of dilute sulphuric acid (1 : 4). Before use, it should be saturated with pure acetylene. After 3 minutes contact, with continuous shaking, the gas is again transferred to the burette and measured. One-fourth of the loss in volume equals the hydrogen phosphide.

L. DE K

Estimation of Ethereal Oils in Aromatic Waters. By HEINRICH BECKURTS and G. FRERICHs (*Chem. Centr.*, 1897, ii, 716; from *Apoth. Zeit.*, 12, 563—564).—The ethereal oil is extracted with ether, the liquid concentrated to 10—15 c.c., and the remainder of the ether removed by passing a current of dry air over it until the ice which always forms has disappeared. In this manner, the amount of oil in fennel and peppermint waters was found to be 0.06 per cent. On account of the very limited solubility of ethereal oils, the so-called concentrated waters invariably contain alcohol.

L. DE K.

Method for Estimating Chloroform in Viscera. By ANTON SEYDA (*Chem. Centr.*, 1897, ii, 815; from *Zeit. offentl. Chem.*, 3, 333—337).—The viscera, after being cut up, are introduced into a distilling flask, made into a thin paste with water containing tartaric acid, and the chloroform distilled off by heating on a sand bath

and passing in steam. The vapours are passed through a condenser and then collected in a 50 c.c. flask; when three parts filled, the receiver is changed and the distillation is stopped when the distillate no longer gives any chloroform reaction. The mixed distillates are then made up to 50 c.c., and in 10 c.c. the chloroform is estimated colorimetrically, five cylinders containing various known weights of chloroform being used for comparison.

The colorimetric estimation is conducted as follows: 1.4 grams of chloral hydrate (= 1 gram of chloroform) is dissolved in a litre of water; before use this is diluted to 10 times its bulk. A 10 per cent. aqueous solution of resorcinol and a 25 per cent. aqueous soda are also prepared; 1 to 10 c.c. of the chloral solution is mixed with 2 c.c. of the resorcinol and 1 c.c. of the soda solution; and the tubes containing this and the unknown solution are heated in the water bath for 10 minutes at 80°, when the red coloration due to the reaction between the resorcinol and the chloroform will have fully developed.

L. DE K.

Estimation of Methylic Alcohol in Ethylic Alcohol. By A. LAM (*Zeit. angew. Chem.*, 1898, 125—130).—Twenty-five c.c. of the spirit, the sp. gr. of which should be about 0.935, is treated in a distilling flask with 5 grams of amorphous phosphorus and 40 grams of iodine. When the action is over, the contents are distilled and the iodides formed are first washed with weak aqueous soda, then with water, and finally dried over calcium chloride. After noting the volume, the sp. gr. is carefully taken, and the amount of methylic iodide ascertained by referring to the tables given in the original paper.

The sp. gr. of methylic iodide is 1.9444; that of ethylic iodide 2.2677.

L. DE K.

Fehling's Solution. By OTTO ROSENHEIM and PHILIP SCHIDROWITZ (*Chem. News*, 1898, 7, 97).—With reference to Jovitschitsch's statement that mineral acids reduce Fehling's solution (this vol., ii, 98), the authors have failed to observe any such reduction either when following Jovitschitsch's directions, or when boiling 25 c.c. of freshly prepared Fehling's solution for 1 minute with hydrochloric, sulphuric, or nitric acid, or when a constant volume of the solution was first acidified with a slight excess of hydrochloric, sulphuric, nitric, or tartaric acid and fresh Fehling's solution added until the reaction was distinctly alkaline to litmus; under the latter conditions, the solutions remained perfectly clear in the cold, but on boiling a slight turbidity not increased by vigorous boiling for 4 minutes was produced, and was due to the separation of a small quantity of hydrated cuprous oxide mixed with organic matter; after the removal of this by filtration, the solution did not give a further precipitate when again boiled.

D. A. L.

Estimation of Lactose in Milk. By ALFRED ORTMANN (*Chem. Centr.*, 1897, ii, 814—815; from *Zeit. Nahrungsm. Hyg. Waar.*, 11, 265—266).—Obermayer recommended precipitation of the proteids in milk by means of trichloroacetic acid and subsequent estimation of the

lactose by precipitation. The author has compared this method with the process used by Soxhlet, who precipitates the proteids by copper sulphate and then estimates the lactose gravimetrically by means of Fehling's liquid. The results obtained were very concordant.

L. DE K.

Polarimetric Method for the Estimation of Starch in Flour, &c. By EDWIN DOWZARD (*Chem. News*, 1898, 77, 107—108).—A malt extract is used capable of transforming an equal weight of potato starch (as mucilage) into dextrin and maltose in 20 minutes at 40·5°. Fifty grams of the extract is dissolved in 500 c.c. of cold water, 5 grams of washed kaolin added, and the mixture agitated and filtered. A gram of flour is mixed with a small quantity of cold water, then with 35 c.c. of boiling water and kept at 100° for 30 seconds, cooled to 48°, treated with 20 c.c. of the clear malt solution, maintained at 48° for 20 minutes, heated just to the boiling point, and filtered. The filtrate is made up to 100 c.c., some kaolin added, the whole filtered, and the clear solution examined in a 20 cm. tube in an instrument of the Laurent half-shadow type, the reading less the rotation due to the malt solution and to any initially optically active matter in the flour gives a number from which the amount of starch is readily calculated.

D. A. L.

Detection of Picric Acid in Beer. By A. RUPEAU (*Chem. Centr.*, 1897, ii, 813; from *Rev. Intern. Falsif.*, 10, 125—126).—Two test-tubes are respectively filled with 10 c.c. of pure beer and beer containing picric acid. To each is now added 1 c.c. of a 2 per cent. solution of potassium cyanide and 1 drop of aqueous soda; the mixture is heated nearly to boiling and the colours are observed. In this manner, 0·01 gram of picric acid per litre may be recognised.

Another test consists in using a reagent composed of 5 grams of iron sulphate, 5 grams of tartaric acid, and 200 c.c. of brine. 0·5 c.c. of the sample is allowed to flow on to 1—2 c.c. of the reagent and 2 drops of ammonia are added and the whole slightly shaken. In the presence of picric acid, a reddish coloration will be noticed. This test will show 0·005 gram of picric acid per litre.

L. DE K.

Preparation of Ammonium Tartrates and Citrates free from Lead. By LEONARD DE KONINGH (*Chem. News*, 1898, 77, 119).—The author finds that lead cannot be removed completely from ammonium hydrogen tartrate by long continued washing or repeated recrystallisation. The best plan of removing lead or copper from ammonium tartrate or citrate is to treat the alkaline solution with hydrogen sulphide as long as the colour intensifies, then agitate with a little kaolin and filter, passing the filtrate through purified animal charcoal to remove any yellowness, and repeating the treatment with hydrogen sulphide and kaolin if necessary. It is not supposed that all the lead or copper can be removed in this manner, but it furnishes a liquid that may be used for comparison in Warington's process.

D. A. L.

The Iodine-addition Method. By J. J. A. WIJS (*Ber.*, 1898, 31, 750—751).—Instead of Hübl's solution for determining the

iodine number of oils, the use of a solution of iodine chloride is proposed. This is made by dissolving 13 grams of iodine in 1 litre of 95 per cent. acetic acid, estimating the oxidising strength of the solution by titration with N/10 thiosulphate, and passing in chlorine gas, washed free from hydrogen chloride, until this oxidising strength is doubled; after a little practice, one can recognise this point by the change in colour. Twenty-five c.c. of such a solution require 56.46 c.c. N/10 thiosulphate; after 96 hours, 56.28 c.c.; and after 72 hours more, 56.27 c.c. This solution is used in the same way as Hübl's reagent, except that less potassium iodide need be added for the titration (10 c.c. of a 10 per cent. solution suffice). The new method gives more constant results than Hübl's, and they are just a little higher. A saving of time is also effected; whereas with Hübl's solution 4 hours are required, with the new solution the addition of the iodine is always complete in 10 minutes, and even in 3—4 minutes in the case of oils with a low iodine number. With specially purified allylic alcohol, and using 75 per cent. excess of the solution, the number 434.1 was obtained after 5 minutes action, and 436.8 after 10 minutes; with Hübl's solution in similar excess, the number 425 was obtained after 20 hours; the theoretical number is 435. C. F. B.

Colour Reaction of Sesame Oil by means of Furfuraldehyde and Hydrochloric Acid. By L. VAN DER GRINTEN and by OSKAR HAGEMANN (*Bied. Centr.*, 1898, 27, 283—284).—The recent German margarine law requires manufacturers to add 10 per cent. of sesame oil to margarine, to enable the latter to be distinguished from butter. Fat containing as little as 0.5 per cent. of sesame oil, when shaken with an equal volume of fuming hydrochloric acid (sp. gr. 1.19) and a few drops of a 2 per cent. alcoholic furfuraldehyde solution, gives a distinct red colour to the hydrochloric acid.

VAN DER GRINTEN (*Milchzeit.*, 1897, 554) remarks that, since it has become known that human urine is used in the production of annatto, other dyes, such as curcuma and coal-tar dyes, have been adopted for the purpose of colouring butter. [Kreusler states that saffron is chiefly employed]. As these dyes give the same colour reaction as sesame oil, butter coloured with them is liable to be rejected as artificial.

HAGEMANN, in reply, points out that the colour reactions cannot be mistaken. Curcuma solutions are coloured by strong hydrochloric acid alone, and on diluting the yellow colour returns.

N. H. J. M.

Colour Reaction of Sesame Oil. By VITTORIO VILLAVECCHIA and GUIDO FABRIS (*Chem. Centr.*, 1897, ii, 772—773).—See this vol., i, 445.

Polimanti's Method of Estimating Fat. By JOSEPH NERKING (*Pflüger's Archiv.*, 1898, 71, 427—430).—In contradiction to Polimanti (this vol., ii, 317), the author maintains that simple extraction with ether does not give a correct result, and that the only trustworthy method is the Pflüger-Dormeyer one, in which a preliminary gastric digestion is performed. W. D. H.

Analysis of Fats. By WILHELM FAHRION (*Zeit. angew. Chem.*, 1898, 267—273).—The author states that when shaking a solution of fat in alcoholic potash with light petroleum to extract any mineral oil, it is advisable to first neutralise any excess of alkali that may be present.

To estimate the amount of unsaponifiable matter in wool grease, 2 grams of the sample is heated in a porcelain basin with 10 c.c. of 2N alcoholic soda, and evaporated to dryness on the water bath, the residue being moistened with strong alcohol and again dried; the dry soap is then dissolved in 70 per cent. alcohol, neutralised with normal hydrochloric acid, and shaken with six successive portions of 20 c.c. of light petroleum. Each time, the latter is washed with 10 c.c. of 50 per cent. alcohol to remove any soap, and the alcoholic liquid returned to the main bulk. The petroleum extractions are mixed, or may be evaporated separately; the last portion should then yield but a mere fraction of residue.

Alcoholic solutions of soap yield a small quantity of soap to light petroleum, particularly in the presence of alkali; this may, however, as stated, be removed by washing with dilute alcohol. Dry soap, whether neutral or alkaline, seems quite insoluble in light petroleum.

The author has also experimented on the solubility of light petroleum in dilute alcohol. If the alcohol is diluted to 70 per cent., the solubility is practically nil, but if soap is present to the extent of 10 per cent., every 10 c.c. of the liquid dissolves 1 c.c. of light petroleum. This fact explains the great difficulty experienced in completely freeing the soapy liquid from unsaponifiable matter by agitating with light petroleum. If difficulty is experienced in the separation of the two layers, this may be remedied by adding more alcohol; more petroleum then, however, passes into the alcoholic liquid, and the shaking must be more frequently repeated. The author now proposes to combine the estimation of unsaponifiable matter with the taking of the saponification number. Three to four grams of the fat is dissolved in 25 c.c. of light petroleum and 25 c.c. of approximately normal alcoholic potash (free from water) is added. After remaining overnight, phenolphthalein is added and the liquid carefully neutralised with N/2 hydrochloric acid, and the saponification number calculated from the result. The liquid is now put into a separating funnel, and sufficient water is added to reduce the alcohol to half strength. Any mineral oil is then extracted by repeated agitation with light petroleum as directed.

A table is given showing the percentage of unsaponifiable matter in several fats and oils. Strange to say, ordinary resin, or colophony, contains no less than 3.85 per cent. of unsaponifiable matter, whilst resin-oil is credited with nearly 20 per cent. of saponifiable matter.

A delicate test is given for the presence of cotton-seed oil in lard. The unsaponifiable matter obtained from 3 grams of the sample is dissolved in 5 drops of acetic anhydride and 2 drops of sulphuric acid, when the adulteration will be proved by the appearance of a blue coloration changing to green.

L. DE K.

Estimation of Alkaloids in White Hellebore. By CH. H. LAWALL (*J. pharm.*, 1897, [vi], 6, 362).—Ten grams of white hellebore,

25 grams of chloroform, 75 grams of ether, and 10 grams of 10 per cent. aqueous ammonia are introduced into a dry flask, and the mixture is vigorously shaken, and allowed to remain for 6 hours, or, still better, overnight; 5 c.c. of 10 per cent. aqueous ammonia is then added, the whole well shaken, and 5 c.c. of the clear solution transferred to a separating funnel. The alkaloids are removed by extracting with three portions of acidified water (each 20 c.c.), these extracts being then placed in a separating funnel, rendered alkaline with ammonia, and agitated with a mixture of chloroform (3 vols.) and ether (1 vol.); the extract is run into a tared flask, the solvent distilled off, and the residue weighed. The amount of alkaloids present seems to vary from 1.12 to 1.25 per cent.

J. J. S.

Estimation of Hæmoglobin in Cat's Blood. By EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1898, 24, 545—547).—The estimation of hæmoglobin in cat's blood is difficult, because it is hard to obtain crystals of it. To the red corpuscles freed from serum, only an equal volume of water must be added, whereas in the case of dog's blood double, and in the case of horse's blood treble, the quantity must be employed. Crystals can also be obtained by the addition of alcohol in the cold. In estimating cat's hæmoglobin colorimetrically, it was found that solutions which gave the same intensity of colour as solutions of dog's hæmoglobin contained practically the same amount of pigment.

W. D. H.

Application of Glan's Spectrophotometer in Animal Chemistry. By AUGUSTIN WRÓBLEWSKI (*Chem. Centr.*, 1897, ii, 532; from *Anzeig. Akad. Wissensch.*, 96, 386—389; 389—390).—*Estimation of Oxyhæmoglobin in Blood.*—The author has experimented with Glan's apparatus to test the blood of dogs, cats, and human beings. If the amount of hæmoglobin is between 0.06 and 0.2 per cent., the absorption-constant may be taken as 0.0015. On dilution, this figure first becomes less, but, on further diluting, it again slightly increases. The observed region of the spectrum is $\lambda = 554$ to 545. On dilution, the absorption-constant in the region of hæmoglobin falls from $\lambda = 562.5$ to 554, but it gets higher in the region of oxyhæmoglobin. The author found that the amount of oxyhæmoglobin is much increased after a night's rest. The proportion of hæmoglobin in a pregnant dog gradually sunk from 12.88 to 6.21 per cent., but the blood of the pups contained 14.22 per cent.

Estimation of Thiocyanates in Saliva.—The author uses a solution of ferric chloride in hydrochloric acid of 1.4 per cent. strength, when the absorption-constant equals 0.00001022.

L. DE K.

Detection of Urobilin and Biliary Pigments. By E. LÉPINOIS (*J. pharm.*, 1897, [vi], 6, 389—390).—A given quantity of zinc chloride and then dilute ammonia, in amount insufficient to redissolve the precipitated zinc hydroxide, are added to the urine. After filtration, the biliary pigments, together with the zinc hydroxide, remain on the paper, whilst the urobilin, if present, is in the alkaline filtrate, which then exhibits a fluorescence and shows the characteristic spectrum. The precipitate is dissolved in acetic acid, and the pigments tested for by Gmelin's method.

J. J. S.

The Precipitation of Proteids. By N. C. HENRIK SCHJERNING (*Zeit. anal. Chem.*, 1898, 37, 73—87; see this vol., ii, 271).—In consequence of the apparent identity of the proteids precipitated by zinc sulphate or by magnesium sulphate, the author has compared the behaviour of his four typical precipitants, stannous chloride, lead acetate, ferric acetate, and uranium acetate, with that of similar salts of related metals. The results show that, under identical conditions, practically equal amounts of nitrogenous matter are precipitated by each member of a group. Thus, lead chloride and stannous chloride, manganic acetate and ferric acetate, precipitate respectively almost exactly equal quantities of nitrogen. On the other hand, metals whose position in the periodic arrangement shows them to be unrelated, as, for instance, magnesium, copper, and ferrous iron used as sulphates, lead, copper, and mercuric chlorides, the same metals and those of the alkaline earths used as acetates, precipitate widely different amounts of nitrogen. The precipitation of the albumins and albumoses by saturating the solution with a sulphate (Mg,Zn) is of a different character, resulting from no chemical reaction, but being simply due to the sequestration of the proteid-solvent by the salt. It is effected by all easily soluble sulphates, including that of sodium. The results tend to confirm the supposition that the substances which exhibit different behaviour with the four typical reagents are really distinct and definite chemical individuals. M. J. S.

Analysis of Gastric Juice. By L. CORDIER (*Compt. rend.*, 1898, 126, 353—356).—The method adopted by the author is based on the fact that lithium chloride is readily soluble in a mixture of equal volumes of absolute alcohol and dry ether, whilst sodium chloride is insoluble. Five c.c. of gastric juice is mixed with a saturated solution of lithium carbonate until alkaline to litmus, evaporated to dryness at 100°, and heated to dull redness with continual stirring, but avoiding unnecessary rise of temperature. The object is to obtain a colourless, or practically colourless, solution. After cooling, the residue is treated with successive quantities of a mixture of equal volumes of alcohol and ether, about 60 c.c. being necessary to completely dissolve the lithium chloride. The solution contains the chlorine of the free hydrochloric acid and of the combined chlorides, which is estimated in the usual way. The carbonaceous residue is extracted with water containing a small quantity of nitric acid, and the chlorine in this solution is estimated. The sum of the two quantities is, of course, the total chlorine.

Free hydrochloric acid is estimated by means of N/10 sodium hydroxide solution, with the phloroglucol-vanillin reagent as indicator.

This method, when applied to gastric juice of various types, gives results very similar to those obtained with the older method of Hayem and Winter. It is rapid in execution, and requires only a small quantity of material. C. H. B.

General and Physical Chemistry.

Action of Light. I. Physical Changes induced by Light. By MAX ROLOFF (*Zeit. physikal. Chem.*, 1898, 26, 337—361).—The physical changes caused by light may be divided into changes in the relative position of (1) the atoms, (2) the molecules. Examples of the first class are collected, and show that the general nature of the change is from a maleinoid to a fumaroid form, the original compound possessing in all cases the greater solubility and lower boiling and melting points. The second class of changes are those of polymerisation, in which, however, the actual formation of double or multiple molecules is not necessary, but only a greater volume concentration of molecules. In all these cases, and a large number of examples are adduced, the polymeride is distinguished from the monomeride by (1) smaller vapour pressure, (2) higher melting and boiling points, (3) smaller solubility, (4) lower specific heat; its formation is always exothermic, and by increase of temperature it is again converted to the monomeride. In changes induced in organic compounds it is noticeable that the change is always associated with a double or treble linking, and the author considers that the action of light cannot be regarded as a mere mechanical disturbance of the molecule, but that the explanation must be sought in the influence of electromagnetic waves on axes of electrical polarity of the molecules. Luminescence is frequently associated with the polymerisation and the reverse change, and both phosphorescence and fluorescence appear to be due to the formation of polymerides which are reconverted to the monomerides with luminescence. The crystal colorations are probably due to similar causes, and in the case of sodium and potassium chloride are connected with the production of trivalent chloride. In many cases, the phenomena occur best in the presence of small quantities of impurities, and the author considers the effect of the latter to be that of a 'sensitiser,' but full consideration is postponed.

L. M. J.

Spectrochemistry of Nitrogen. VII. By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1898, 26, 47—76. Compare this vol., ii, 362).—A further discussion of the bearing of the author's spectrometric observations on the constitution of various nitrogen compounds which had been examined in solution. *Nitrosobenzene* has the constitution $C_6H_5 \cdot N \cdot O$ in benzene solutions, but in alcoholic solutions it is probable that association occurs. *Tetramethylethylenenitrosyl chloride* does not contain the $\cdot N \cdot O$ group, and has probably a ring constitution for which the author proposes two forms. In the case of *phenylhydroxylamine*, the results are doubtful, but indicate a constitution analogous to that of hydroxylamine itself, that is, $NHPh \cdot OH$, in preference to $NH_2Ph \cdot O$. *Paranitrodiazobenzene methylic ether* (Abstr., 1894, i, 282) belongs to the series of isodiazotates, and has the constitution $NO_2 \cdot C_6H_4 \cdot N \cdot N \cdot OMe$. *Nitrourethane*, partly on physical but partly on chemical grounds,

is considered to be $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\begin{array}{c} \text{O} \\ \diagup \text{N} \diagdown \\ \text{H} \end{array}\text{N}$. From the examination

of *benzenediazoic acid* and its substitution derivatives, the value of the N_2O_2 group is found to be slightly greater than in the aliphatic nitramines, and the increase is ascribed to the influence of the solvent and of the phenyl group. The constitution proposed by Hantzsch (Abstr., 1894, i, 456) would yield much lower values, and the acid

hence possesses the nitramine constitution, that is, $\text{NHPh}\begin{array}{c} \text{O} \\ \diagup \text{N} \diagdown \\ \text{O} \end{array}\text{N}$.

Derivatives of primary and secondary *nitramines* and *isonitramines* showed that in each class the spectrometric values of the group N_2O_2 were identical, and the author considers as probable the following

formula, $\begin{array}{c} \text{R} \\ \diagup \text{N} \diagdown \\ \text{H} \end{array}\begin{array}{c} \text{O} \\ \diagup \text{N} \diagdown \\ \text{O} \end{array}\text{N}$, primary nitramines; $\text{OH}\cdot\text{NR}\cdot\text{N}:\text{O}$ isonitramines, and the differences in the two series of isonitramine derivatives

are to be ascribed to differences in the configuration with respect to the nitrogen atom. L. M. J.

Influence of X-Rays on the Luminosity of Gases. By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1898, 26, 165—169). —When a tube containing gas, at low pressure, is exposed to electrical oscillations, it becomes luminous when the pressure is reduced sufficiently, but if exposed also to the influence of X-rays the pressure at which luminosity occurs is increased. This effect of the rays was examined quantitatively, and the subjoined table gives the pressure at which the gas becomes luminous (I) by the oscillations alone, (II) by the simultaneous action of X-rays; (III) gives the percentage increase of pressure.

	Molecular wt.	I.	II.	III.
Hydrogen.....	2	71 mm.	94 mm.	32·4
Oxygen.....	32	51 "	68 "	33·3
Methylic alcohol.....	32	17·5 "	27·5 "	57·1
Ethylic alcohol.....	46	16·5 "	26 "	57·5
Ethylic ether.....	74	14 "	24 "	64·3
Chloroform	119	10 "	18 "	80

The influence of the X-rays increases with the molecular weight and molecular complexity of the gas. The author does not consider the effect to be due to decomposition into atoms, or ions, and advances, with reserve, the hypothesis that a certain mobility is imparted to the ether by the rays, and this causes acceleration of the intramolecular oscillations, and hence, under the influence of the electrical oscillations, causes dissociation of some molecules, and brings about a multitude of

minute discharges from molecule to molecule. As the luminous gas in a vacuum tube has conducting properties, the author considers it possible that it also, like metals, would absorb the X-rays, but experiments show that this was not the case, the luminous tube being as transparent in this respect as a non-luminous tube. L. M. J.

Validity of Maxwell's Equations. By ANTON SCHEYE (*Zeit. physikal. Chem.*, 1898, 26, 159—160).—The author upholds the validity of Maxwell's equations, and points out two sources of error in Wedell-Wedellsborg's paper on this subject (this vol., ii, 61); of these the more important is that in the equations expressing the conservation of energy during the induction phenomena, the energy of the electric current was entirely neglected. L. M. J.

Oxidation and Reduction Chains, and the Influence of Complex Ions on the Electromotive Force. By RUDOLF PETERS (*Zeit. physikal. Chem.*, 1898, 26, 193—236).—If a mercury electrode be employed in a mixture of ferrous and ferric salts, a reaction proceeds in accordance with the equation $\text{Hg} + \text{Fe}^{+++} + \text{Cl}^- = \text{Fe}^{++} + \text{HgCl}$. For any concentration the potential is given by the expression $\pi = RT/F \times \log. C_2 c_3 / C_3 c_2$, where C_2/C_3 is the equilibrium ratio of the ferrous to ferric ions, and c_2, c_3 the actual concentration of these ions; this may be written $\pi = A + 0.0575 \log. c_3/c_2$, and the value of A may be obtained directly by making $c_3 = c_2$ or by calculation from the E. M. F. at any concentration, and the values so obtained from the E. M. F. of a number of very different mixtures agreed very closely and corresponded with an equilibrium ratio $k = 10^{4/0.0575} = 10^{7.50}$, which is hence the ratio of the numbers of ferrous and ferric ions when the solution is in equilibrium with the normal electrode. (Complete or equal dissociation of the two ion salts is assumed in the calculation.) By the addition of potassium chloride, the value of k was diminished, the mean value obtained being $10^{7.15}$. In neutral solutions, the potential was found to vary considerably with dilution, but this was not the case in acid solutions or solutions containing potassium chloride. Solutions in a normal sodium nitrate solution gave values almost identical with those in pure water, so that ferric chloride and ferric nitrate are equally dissociated. In the case of mixtures of ferric and ferrous sulphates, the value of k was found to be $10^{6.6}$, so that at equal concentrations ferric sulphate gives fewer ferric ions than the chloride. Experiments with chromous and chromic compounds, and with manganous and manganic compounds, gave no quantitative results, as constant values could not be obtained. The van't Hoff expression employed for the ion chain was, however, found to be at least qualitatively correct. Addition of fluorine ions in all cases raises the reduction potential, and this effect was further examined. The conductivity of mixtures of iron salts with sodium fluoride is less than the sum of the conductivities of the constituents, the difference being greatest with ferric compounds, in which case also it increases with dilution. The ferric salts, therefore, probably form complex compounds with the sodium fluoride, a view further supported by freezing point determinations. By the addition of sodium fluoride to the mixed ion salts

the E. M. F. falls greatly; thus, in the case of a mixture of N/10 ferrous and ferric salts the addition of an equal volume of 3N/10 solution of sodium fluoride caused the E. M. F. to become negative, or decreased the concentration of the ferric ions to $10^{-7.5}$ of its former amount. A white salt is also precipitated by the fluoride, and the composition was found to be $\text{Na}_3\text{FeF}_6 + \frac{1}{2}\text{H}_2\text{O}$. This was proved to be a complex salt in which the iron is present in the anion, as by electrolysis the percentage of iron increased at the anode and decreased at the cathode. It is probable that the reduction of the E. M. F. by addition of sodium fluoride is due to the formation, not only of the slightly dissociated ferric fluoride, but also of this salt.

L. M. J.

Chemical Equilibrium and Electromotive Force. By CARL KNÜPFER (*Zeit. physikal. Chem.*, 1898, 26, 255—284).—In the galvanic chain, thallium in thallium chloride | potassium chloride | potassium thiocyanate | thallium in thallium thiocyanate | the reaction may be represented by $\text{TlCl} + \text{SCN}^- = \text{Cl}^- + \text{TlSCN}$, and if the ratio of the equilibrium concentrations of chlorine and thiocyanate ions = k and the ratio of these ions actually present = a , then the electromotive force is given by the expression $\pi = RT/F \cdot \log. k/a$. From determinations of the E. M. F., therefore, the ratio of the equilibrium concentrations may be calculated. The values so obtained were compared with those obtained chemically, the numbers being

Temperature.	Electrically found ratios.		Chemically found ratio.
39.9°	0.87	0.88	0.85
20.0	1.27	1.25	1.24
0.8	1.77	1.82	1.74

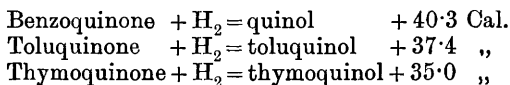
The above reaction is attended with the heat development of +31.8*K* and from this the temperature coefficient of the equilibrium constant may be deduced by the expression $\log. K_2 - \log. K_1 = q/R(1/T_1 - 1/T_2)$ and the temperature coefficient of the E. M. F. by the expression $(\pi - q)T = d\pi/dT$. The values $K_{20}/K_{39.9}$ and $K_{0.8}/K_{39.9}$ so obtained agree well with the chemically found values, and the temperature at which $K=1$ is found to be (1) 31.2°, (2) 32.5°, whilst the temperature at which the change in direction of the current occurs agrees well with the found temperature in each of the galvanic chains examined.

L. M. J.

Quinones and Quinols. By AMAND VALEUR (*Compt. rend.*, 1897, 125, 872—874).—The following thermochemical data have been obtained for various quinones and quinols.

	Melting point.	Heat of combustion		Heat of formation.
		at constant volume.	at constant pressure.	
Benzoquinone			656.8 Cal.	+47 Cal.
Toluquinone	68°	805.05 Cal.	805.3 "	+61.8 "
Thymoquinone.....	45	1273.4 "	1274.6 "	+82.4 "
Quinol			685.4 "	+87.3 "
Toluquinol	126	836.3 "	836.9 "	+99.2 "
Thymoquinol	139	1308.1 "	1308.6 "	+117.4 "

The difference between the heats of formation of toluquinone and benzoquinone (14.8 Cal.) is much greater than that between the heats of formation of toluene and benzene (namely 6.4 Cal.). The difference between a quinone and the corresponding phenol, with the exception of the first members of the two series, appears to be about 6 Cal.; for example, thymol = 76 Cal., thymoquinone = 82.4 Cal.



J. J. S.

Behaviour of Atmospheric Air and of Chemically Prepared Gases at about 350—500° under Atmospheric Pressure. By H. TEUDT (*Zeit. physikal. Chem.*, 1898, 26, 113—131).—The author describes the air thermometer at constant pressure which was used in the experiments, and investigates the probable sources and extent of the experimental errors. Temperatures were taken by a Jena glass thermometer, graduated to 550° and having the upper space filled with nitrogen. Atmospheric air from the laboratory and from the open showed in all cases a very marked increase of expansion at temperatures above 350°, the difference between the observed and calculated volumes reaching about 2 per cent. at 400° and 3 per cent. at 450°. Similar results were obtained with air which had been freed from oxygen and carbonic anhydride. Chemically prepared oxygen and nitrogen, however, gave results in almost complete accord with Gay Lussac's law. The differences found with the air cannot be due to moisture, as the other gases were also moist, and it is very improbable that they could be occasioned by the small quantity of argon which is present. To explain the results, it is necessary for about 8 per cent. of the air to be dissociable into 2 atoms or 6 per cent dissociable into 3 atoms. Air collected immediately after rain did not show the effect, so it appeared probable that the dissociable portion is more soluble in water, and the author therefore attempted to concentrate it by collecting the gases dissolved in water. A greater divergence from Gay Lussac's law was thus obtained, and a similarly more concentrated product appeared to be obtained by diffusion. The author considers that these results indicate a probable allotropic modification of nitrogen, the existence of which is also probable from the relationship of that element to phosphorus.

L. M. J.

Vapour Pressure of Homogeneous Mixtures. By F. DOLEZALEK (*Zeit. physikal. Chem.*, 1898, 26, 321—336).—The work necessary to transport 1 gram equivalent from a dilute to a concentrated solution may be also determined from that necessary to distil the solvent in the reverse direction and an expression may be thus obtained for the E. M. F. of a concentration chain. By equating the two values of the E. M. F.

thus obtained, the equation $n_2 \log. p_2 - n_1 \log. p_1 - \int_{n_1}^{n_2} \log. p dn = \log. \pi_2/\pi_1$

is obtained which reduces to $\pi_2/\pi_1 = p_2^{n_2}/p_1^{n_1} e - \int_{\pi_1}^{\pi_2} \log. p dn$ where

p_1, p_1 are the partial pressures of the solvent, n_2, n_1 the number of molecules of solvent for 1 molecule of solute, and π_2, π_1 the partial pressures of the solute. If electrodes reversible with respect to the solvent be employed, a corresponding expression for p_2/p_1 is obtained. Hence the partial pressure curve of the solute may be obtained from that of the solvent, and *vice versa*. The author describes fully the apparatus and method employed for the determination of the partial pressures and the E. M. F., and the values obtained for the latter are compared with those calculated as indicated, the agreement being very satisfactory. The relative pressures of sulphuric acid and water in various mixtures was determined, and it was found that the ratio sinks very rapidly on dilution, being 1 at 58.4 per cent. and 2×10^{-4} at 35.8 per cent. The author further deduces from the above equations the simple relation $d \log. \pi/d \log. p = n$.

L. M. J.

Demonstration of the Ludwig Phenomenon. By RICHARD ABEGG (*Zeit. physikal. Chem.*, 1898, 26, 160—164).—The Ludwig phenomenon is the term applied to the diffusion of a dissolved substance from places of higher to places of lower temperature in a solution, an effect ascribed by Van't Hoff to the greater osmotic pressure at higher temperatures. This phenomenon may be demonstrated by enclosing a vessel containing the solution in a glass mantle, through the lower portion of which cold water circulates while the upper part is heated by a current of steam. If the solution is saturated for the lower temperature, then as the solute diffuses from the hotter portions, crystals form and grow in the cold liquid, and this may be well observed in a couple of hours with sodium chloride, potassium iodide, copper sulphate, and other salts. No quantitative measurements were made, but it is doubtful whether Van't Hoff's explanation is sufficient, and the author suggests that the hot and cold water may also partially act as different physical liquids.

L. M. J.

Non-electrolytic Dissociation of Water in Aqueous Ethylic Alcohol. By ROBERT LUTHER (*Zeit. physikal. Chem.*, 1898, 26, 317—320).—The dissociation constants of water in two solvents are given by the equations $K_A(\text{H}_2\text{O})_A^2 = (\text{H}_A)^2\text{O}$, and $K_B(\text{H}_2\text{O})_B^2 = (\text{H}_B)^2\text{O}_B$, where the symbols represent the active masses of the constituents in solvents *A* and *B*. The ratios of the active masses of the gases are given by their solubilities in the two solvents, and that of the active masses of water by its partial vapour pressure in the two liquids, and hence the ratio K_A/K_B can be obtained. The author calculates this ratio for various mixtures of ethylic alcohol and water, and finds that it at first decreases until the percentage of alcohol reaches about 25 per cent., when it increases very rapidly. The concentration of hydrogen and oxygen in water vapour at 20° is calculated as 10×10^{-27} and 5×10^{-27} molecules per litre respectively.

L. M. J.

Solubility of Iodine in Mixed Solvents. By LUDWIK BRUNER (*Zeit. physikal. Chem.*, 1898, 26, 145—151).—The solubility of various compounds in water is lowered by the addition of alcohol, and the hypothesis is largely accepted that the alcohol abstracts some of

the water with the formation of hydrates. Bodländer found this hypothesis was not supported by facts, and that when the solid was insoluble in one of the solvents the expression $W \sqrt[3]{S} = \text{constant}$ represents the solubility, where w = percentage of water, and s that of the salt. The author has therefore investigated the less complicated case of the solubility of iodine in mixtures of solvents, the values obtained being compared with those calculated by the mixture rule. Mixtures of benzene, carbon bisulphide, chloroform, carbon tetrachloride, ethylic alcohol, and normal propylic alcohol were investigated, and diagrams are given showing the results obtained. With the sole exception of the mixture of 90 per cent. benzene with 10 per cent. chloroform, the values are lower than those calculated, and the greatest differences are obtained in the case of alcoholic mixtures. The previously observed case of aqueous alcohol is therefore probably but an example of a general law. If a dilute solution of potassium iodide be regarded as a mixture of a concentrated solution with water, it follows that the solubility of iodine in this solvent should increase more rapidly than the percentage of potassium iodide and this is found to be the case, the ratio I/KI being a function of the potassium iodide concentration.

L. M. J.

Proof of the Theory of the Solubility of Salts consisting of Three Ions. By ARTHUR A. NOYES and E. HAROLD WOODWORTH (*Zeit. physikal. Chem.*, 1898, **26**, 152—158).—In the case of salts consisting of two ions, the influence of an admixed salt with one similar ion on the solubility has been proved to be in accord with the theory $k_1 \times k_2 = \text{constant}$, where k_1 and k_2 are the concentrations of the two ions. In the case of salts of three ions, a complete proof of the expression $k_1 \times k_2 = \text{constant}$ has not been obtained, and the author therefore attempted to verify this equation by the determination of the solubility of lead iodide in water and in very dilute solutions of potassium iodide and of lead nitrate. Owing to the extreme dilution, the salts are almost completely dissociated, so that dissociation changes do not occur to complicate the results. The solubility determinations were done by the conductivity method, which has the advantage of giving directly the number of ions. If m_0, a_0 are the solubility and dissociation of lead iodide in water and $m_1 a_1, m_2 a_2$ the corresponding values for the lead iodide and potassium iodide in the mixed solution, then $m_1 a_1 (m_1 a_1 + m_2 a_2)^2 = m_0^2 a_0^3$ and as $m_2 a_2$ and $m_0 a_0$ are known, the values for $m_1 a_1$ are obtained by approximations. For the lead nitrate solutions the expression $(m_1 a_1 + m_2 a_2) m_1^2 a_1^2 = m_0^3 a_0^3$ holds, and the values for $m_1 a_1$ in this case may be similarly obtained. The calculated values agree very closely with the determinations, so that for lead iodide the solubility law stated is valid.

L. M. J.

The Hydrolysis of the Ethereal Salts of Dibasic Acids. By OSC. KNOBLAUCH (*Zeit. physikal. Chem.*, 1898, **26**, 96—108).—The hydrolysis of the ethereal salts of a dibasic acid must not be regarded as a reaction of the second order, but as taking place in two stages, (1) the hydrolysis to the acid ethereal salt, (2) the further hydrolysis

of this to the acid, and the composition at any time will, therefore, be a function of two velocity constants, not of one only. The theoretical investigation of this subject has been worked out by Ostwald (*Lehrbuch der Allg. Chem.*, 2, part ii, 277), and in order to verify the equations there obtained the author has investigated the hydrolysis of ethylic succinate by sodium hydroxide. If C_1 , C_2 , C_3 , and C_4 represent the concentration of alkali, ethereal salt, acid salt, and sodium succinate respectively, then $dC_1/dt = -k_{1.2}C_1C_2 - k_{1.3}C_1C_3$, and as in the initial stages C_3 , and the final stages C_4 , is negligible, it follows that observations at the commencement and end of the hydrolysis give the values for $k_{1.2}$ and $k_{1.3}$ respectively. The values so obtained are almost constant, and from them the composition at intermediate stages is calculated and found to agree well with the observations, so that Ostwald's equations for the two-stage hydrolysis may be regarded as experimentally verified.

L. M. J.

Equilibrium in the System—Water, Benzoic Acid, and Ethylenic Cyanide. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1898, 26, 237—254).—The above system differs from others previously examined in the fact that of the three pairs of liquids, only one, benzoic acid and ethylenic cyanide, forms a homogeneous mixture, whilst the other two pairs form two liquid layers only within definite temperature limits, namely, 18.5—56.5° for water and ethylenic cyanide, and 95—115.5° for water and benzoic acid. The equilibrium curve for the last pair has been determined by Alexéeff, and may be divided into three parts: (1) liquid 1 + solid acid; (2) liquid 1 + liquid 2; (3) liquid 2 + solid acid; the critical temperature for the two liquid phases is 115.5°. The equilibrium curve for water and cyanide was previously determined by the author (*Abstr.*, 1897, ii, 483), and the remaining curve for benzoic acid and the cyanide was therefore determined, and the composition of the liquid in equilibrium with each solid phase is given. In the case of the equilibrium of the three compounds, the cryohydric point for ice-cyanide-acid liquid is a little below -1.2°, and here three equilibrium curves meet, of which two are ice curves, the third being that of cyanide-acid-liquid, and the composition of the liquid phase at different temperatures is determined. On this curve the quintuple point for cyanide-acid-liquid 1 and liquid 2 occurs at 11—12°, and the composition of the two liquid phases was determined. Representing the more aqueous phase by liq. 1, increase of temperature causes the change liq. 1 + cyanide + acid \rightarrow liq. 2, and at the quintuple point four curves meet, of which one, namely, that for acid + liq. 1 + liq. 2 is interesting inasmuch as the equilibrium occurs from 11.5° to 51° and again from 87° to 96°, but not in the interval 51—87°, as at the lower of these two temperatures the composition of the two liquid phases becomes identical. From the equilibrium curves with a solid benzoic acid phase, it is seen that the solubility in certain mixtures of cyanide and water is greater than in either constituent. The other equilibrium curves are traced, and the necessary diagrams are given in the paper.

L. M. J.

Velocity of Crystallisation. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1898, **26**, 307—316).—The author describes the differences in the structure and habit of the crystals produced with various degrees of undercooling, and hence various velocities of crystallisation. At first clear crystals form irregularly, then at those temperatures where the velocity increases with the undercooling, the crystals form parallel to the long axis of the tube and enclose noticeable liquid spaces, but when the velocity of crystallisation is constant the crystallisation is complete, and only air spaces occur due to contraction. The effect of pressure is to diminish the crystallisation velocity, the constant for benzophenone being decreased in the ratio 1:0.96 by a pressure of 300 atmospheres. The author calculates the temperature at which the heat evolved by crystallisation is sufficient to raise the whole mass to the melting point by the equation $T = T_0 - r_0/c_m$ where r_0 is the latent heat of crystallisation, c_m the mean specific heat of the liquid between T and T_0 , and T_0 the melting point. Thus, calculated for betol, $T = 45^\circ$, and this should be the temperature at which the crystallisation velocity begins to decrease; the temperature experimentally found was 58° , and this higher value is explained by the fact that the change is not actually adiabatic. The composition of the limiting layer can be calculated by the expression $x = C_m t / r_0$ where t is the undercooling and x the percentage of crystals, the assumption being made that the whole of the limiting layer is brought to the melting point. The variation of the velocity of crystallisation is explained by an assumed influence of the crystals on the liquid, this influence increasing with undercooling until a constant value is reached. The author finally replies to some objections raised by Küster (this vol., ii, 330) against the assumption that the melting point temperature always prevails in the limiting layer of crystallisation. L. M. J.

Inorganic Chemistry.

Simple Method for the Preparation of Diazoimide. By MAXIMILIANO DENNSTEDT and WILHELM GÖHLICH (*Chem. Zeit.*, 1897, 21, 876—877).—When a dilute solution of diazoimide is oxidised, in an atmosphere of carbonic anhydride, with potassium permanganate and sulphuric acid, the only gaseous product is nitrogen.

The best method of obtaining diazoimide from hydrazine is to treat the sulphate, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$, with nitrous acid. A much better yield, namely, 0.2 gram from 5 grams of the sulphate, is obtained by this method than by that recommended by Curtius (*Abstr.*, 1893, ii, 372). Potassium nitrite (3.3 grams) is dissolved in water (about 200 c.c.), and sufficient sulphuric acid is added to neutralise the free alkali present and also to liberate the nitrous acid; this solution, which is well cooled, is added to a well-cooled aqueous solution of hydrazine sulphate (5 grams), and after the evolution of gas has ceased the

mixture is distilled, when a dilute solution of diazoimide passes over. The gases evolved consist of oxygen, nitrogen, and nitrous oxide.

J. J. S.

Salts of Hydrogen Nitride. By LOUIS M. DENNIS and C. H. BENEDICT (*Zeit. anorg. Chem.*, 1898, 17, 18—25).—*Lithium nitride*, $\text{LiN}_3 + \text{H}_2\text{O}$, prepared by neutralising a solution of lithium hydroxide with hydrogen nitride and allowing the solution to evaporate in the air, crystallises in colourless, lustrous needles, is hygroscopic, and very easily soluble in water or alcohol. When gently heated, it loses its water of crystallisation, and on further heating is decomposed.

Sodium nitride, NaN_3 , prepared in the same way as the lithium salt, separates in clear, colourless crystals. The freshly prepared aqueous solution is neutral, but becomes alkaline after some time. It is not easily decomposed by heat, and can be maintained molten for several hours without undergoing decomposition.

Potassium nitride, KN_3 .—The freshly prepared solution rapidly becomes alkaline; the crystalline salt is obtained by allowing the solution to evaporate by exposure to air, and adding a few drops of hydrogen nitride from time to time so as to maintain a slightly acid reaction. It melts when heated, is decomposed only at a high temperature, and is sparingly soluble in alcohol, so that it can be precipitated from the aqueous solution by the addition of alcohol.

Rubidium nitride, RbN_3 , crystallises in slender needles, is extremely soluble in water, from which solvent it is precipitated by the addition of alcohol, melts when gently heated and decomposes at a higher temperature with an explosion and evolution of light.

Cæsium nitride, CsN_3 , obtained by allowing the solution to evaporate over sulphuric acid, crystallises in colourless needles, is extremely soluble in water, insoluble in alcohol, and decomposes only when heated to a high temperature.

All the alkaline nitrides are stable on exposure to air except the lithium salt, which gradually decomposes. None of the salts are explosive, and the tendency to decompose by heat decreases with increase of the atomic weight of the base. They resemble the chlorides of the alkalis in their solubility in water, and the solubility increases with the atomic weight of the base; the solubility in alcohol varies in the reverse direction to that in water.

Calcium nitride, CaN_2 , prepared by dissolving calcium oxide in a dilute solution of hydrogen nitride and then evaporating over sulphuric acid, crystallises in white aggregates, decomposes when heated in solution on the water bath, and when heated alone explodes somewhat violently. *Strontium nitride*, SrN_2 , resembles the calcium salt. *Barium nitride*, $\text{BaN}_2 + \text{H}_2\text{O}$, forms lustrous crystals, and decomposes with a loud explosion when heated. The nitrides of the alkaline earths are all soluble in water, the solubility decreasing with increase in the atomic weight of the base. When exposed to the air they become alkaline, and in aqueous solution gradually evolve hydrogen nitride. The crystallographic examination of the salts shows that the lithium and sodium salts crystallise in the hexagonal system, the potassium,

rubidium, and caesium salts in the tetragonal system, the calcium and strontium salts in the orthorhombic, and the barium salt in the triclinic system.

E. C. R.

Catalytic Influence of various Gases and Vapours on the Oxidation of Phosphorus. By M. CENTNERSZWER (*Zeit. physikal. Chem.*, 1898, 26, 1—46).—The luminosity and oxidation of phosphorus in air or oxygen only occurs when the pressure is reduced to a quantity which is a function of the temperature, and is also affected by the presence of other gases. According to Joubert's results, the luminosity pressure of oxygen is a linear function of the temperature, two sets of experiments having given the results. (1) $P = 270 + 19.57t$, (2) $P = 320 + 23.19t$, whilst, further, the partial pressure of oxygen is a linear function of the percentage volume concentration of the admixed gas, being given by the equation $p_x = p_0 - Ax$; all gases hence reduce the necessary oxygen pressure, but to different extents, the magnitude of the constant A differing for the various gases. The author has further studied this effect, employing a large number of gases and vapours at various concentrations, and a full description of the experimental methods is given. An intermittent luminosity was observed when the pressure is a few centimetres above that necessary for continuous luminosity, but this phenomenon was not further investigated. The author finds that the simple formula of Joubert does not hold except for small concentrations, and a quadratic expression $p_x = p_0 - Ax + Bx^2$ is necessary, and the constants A and B are given for all the compounds examined. The agreement between the observed values and those calculated by this formula is, however, far from satisfactory, and the author considers a logarithmic expression would give better results. The value of the constant A appears to increase with the number of carbon atoms and also with double linking. Substituents appear to produce little effect, except iodine, which causes an enormous increase in the constant. The presence of small quantities of ozone increases the luminosity pressure of the oxygen, and the author considers this to be the probable cause of the higher values for the pressure which were obtained by Ewan (*Abstr.*, 1895, ii, 213) and Joubert. The discussion of the nature of the process is postponed.

L. M. J.

Perborates and their Constitution. By SIMEON M. TANATAR (*Zeit. physikal. Chem.*, 1898, 26, 132—134).—The salts of persulphuric and analogous acids are by some chemists regarded as compounds of metallic peroxides with peroxides of negative elements and not analogous to ordinary salts. The heat of decomposition by sulphuric acid was determined in the case of sodium perborate and ammonium perborate, the values obtained being respectively +2.614 Cal. and +3.475 Cal., which indicate a constitution similar to other salts and not a combination of peroxides for which much higher values should be obtained. These salts, which possess powerful oxidising properties, may be produced by the electrolysis of the orthoborate or by its oxidation by means of hydrogen peroxide.

L. M. J.

The Hydrate formed by Potassium Carbonate, and its Dissociation. By HENRI LESCŒUR (*Bull. Soc. Chim.*, 1897, [iii], 17, 18—23).—Measurements of the vapour pressures at 20° and 100° of systems containing potassium carbonate and water in various proportions, indicate the existence of a hydrate of the formula $K_2CO_3 + 2H_2O$. Its dissociation pressure is less than 1.5 mm. at 20° and is 100 mm. at 100°; no other hydrate appears to exist. Experiments made on the dehydration of alcohol by potassium carbonate show that this hydrate is the first compound to be formed, the remainder of the water present uniting with the alcohol in the proportions corresponding with the hydrate $4C_2H_5O, H_2O$, whilst any excess dissolves the hydrated potassium carbonate and forms a solution in which the alcohol is insoluble. The discordant results which the author and other observers have previously obtained in researches on the hydrate of potassium carbonate are attributed to neglect of the influence of carbonic anhydride. Old specimens of the salt which have been exposed to the air may contain 50 per cent. of the hydrogen potassium carbonate. N. L.

Silver Plumbite. By FRIEDRICH BULLNHEIMER (*Ber.*, 1898, 31, 1287—1289).—A compound, $Pb(OAg)_2$, has been obtained by adding excess of a solution of lead nitrate in aqueous potash to a solution of silver nitrate in aqueous potash, with just so much ammonia that no precipitate forms at once when this solution is mixed with the lead solution, about 2 grams of lead nitrate being added for every gram of silver nitrate. The mixture is warmed gently in the water bath, when a crust of small needles with the above composition is deposited. Silver plumbite is brown, and has a black streak; it is stable towards dilute acids and alkalis, but is decomposed by strong acids.

C. F. B.

Double Thiosulphates of Copper and Sodium. By CHANDRA-BHUSHAN BHADURI and IYOTIBHUSHAN BHADURI (*Zeit. anorg. Chem.*, 1898, 17, 1—17).—When solutions of sodium thiosulphate and copper sulphate are mixed and allowed to remain for some time, coloured salts are obtained. The colour of these salts depends on the ratio of the sodium thiosulphate to the copper sulphate, the concentration of the solutions, and the presence of alcohol.

A yellow salt is obtained by mixing saturated solutions of copper sulphate (1 mol.) and sodium thiosulphate (2 mols.) at 20° to 34°, which the authors consider to be a double thiosulphate of the formula $7Cu_2S_2O_3, 5Na_2S_2O_3 + 16H_2O$.

A salt which has approximately the composition $4Cu_2S_2O_3, 3Na_2S_2O_3 + 9H_2O$, but which varies slightly according to the temperature at which it is prepared, is obtained by mixing saturated solutions of copper sulphate and sodium thiosulphate previously heated to 50—60°.

The above yellow salt is also obtained by mixing solutions of copper acetate and sodium thiosulphate in almost any proportion. The reddish precipitate of cuprous hydroxide, which is obtained by the action of sodium hydroxide on the yellow salt, is partially converted into copper sulphide when the mixture is heated to boiling; this is due to the reaction between the cuprous oxide and sodium thiosulphate. The authors find

that cuprous oxide dissolves in sodium thiosulphate when gently warmed according to the equation $\text{Cu}_2\text{O} + \text{H}_2\text{O} + \text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaOH} + \text{Cu}_2\text{S}_2\text{O}_3$. The copper thiosulphate is held in solution by an excess of sodium thiosulphate. Under ordinary conditions, this solution is very unstable, and quickly deposits copper sulphide.

A *white* salt, $9\text{Cu}_2\text{S}_2\text{O}_3 \cdot 5\text{Na}_2\text{S}_2\text{O}_3 \cdot 8\text{NaCl} + 12\text{H}_2\text{O}$, is obtained by adding a concentrated solution of sodium thiosulphate to a solution of copper chloride. It is also obtained in an impure state by dissolving the yellow salt in dilute hydrochloric acid, and precipitating with concentrated acid.

The *salt*, $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 + 2\frac{1}{2}\text{H}_2\text{O}$, is obtained as a yellowish-white precipitate by mixing a concentrated solution of copper sulphate or acetate (1 mol.) with a solution of sodium thiosulphate (2 mols.), and after allowing the mixture to remain for some time adding a large excess of acetic acid; it is very stable when dry, even if exposed to the air.

E. C. R.

Action of an Alkaline Solution of Stannous Chloride on Lead Salts. By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1898, 31, 1118—1119).—When a solution of lead nitrate is treated with stannous chloride and a large excess of 10 per cent. aqueous soda, the precipitate, after it has been freed from tin by washing with cold 5 per cent. sulphuric acid, consists of metallic lead.

C. F. B.

Double Iodide of Lead and Potassium. By FREDERICK C. HUXLEY BROOKS (*Chem. News*, 1898, 77, 191).—When a solution of lead nitrate, containing 1 gram in 10 c.c., is treated with a saturated solution of potassium iodide until the precipitate is just dissolved, and the mixture left standing for a few minutes, a copious, crystalline precipitate forms having the composition $\text{PbI}_2 \cdot 2\text{KI}$. When washed with absolute alcohol and dried between filter papers, it forms silky, acicular, almost white crystals, slightly soluble in boiling chloroform, readily soluble in strong potassium iodide, insoluble in alcohol; when heated gently, it becomes yellow, but resumes its original shade on cooling; if strongly heated, partial decomposition ensues with the evolution of iodine. The most characteristic reaction is its decomposition into lead iodide and potassium iodide by the action of water, this is so sensitive that the moisture of the air is sufficient to effect it in a few minutes, as indicated by the appearance of a yellow coloration.

D. A. L.

Atomic Weights of Praseodymium and Neodymium. By HARRY C. JONES (*Amer. Chem. J.*, 1898, 20, 345—358. Compare Brauner, *Proc.*, 1898, 70).—The atomic weight of praseodymium was determined by converting the peroxide into the sesquioxide by reduction in an atmosphere of hydrogen, and then synthesising the sulphate from the latter oxide. Attempts were made to convert the peroxide directly into the sulphate, and to estimate the sulphuric acid in this salt by precipitation with barium chloride, but as the precipitate always contains praseodymium, the method had to be abandoned (compare Marignac, *Ann. Chim. Phys.*, [iii], 1849, 27, 231; 1853, 38, 151).

A similar method was used in the case of neodymium, but as the oxide is a sesquioxide, reduction in a current of hydrogen was unnecessary.

The oxides used were prepared from the double nitrate of praseodymium or neodymium and ammonium (purified by fractional crystallisation from concentrated nitric acid) by conversion into the oxalate, and subsequent heating.

As a mean of twelve determinations in each case, the value for praseodymium is 140.46 where $O=16$; or 139.41 where $O=15.88$; and for neodymium 143.55 where $O=16$ or 142.47 where $O=15.88$; the difference between the highest and lowest determination in each case being 0.16.

The author compares his results with those obtained by von Welsbach (Abstr., 1885, 1113), and is at a loss to explain that the values appear to be reversed.

		Von Welsbach.			Jones.
Pr.	143.6	...	140.45.
Nd.	140.8	...	143.6.

A. W. C.

NOTE.—This is practically the same result as arrived at by Brauner (*loc. cit.*), who obtained for praseodymium the value 140.95, and for neodymium 143.63.

A. W. C.

Cobalt Nitrite and Cobalt Nitrocyanide Compounds. By ARTHUR ROSENHEIM and IVAN KOPPEL (*Zeit. anorg. Chem.*, 1898, 17, 35—72).—Compounds of the constitution $3R_2O, Co_2O_3, 6N_2O_3$ are obtained by treating a mixture of the theoretical quantities of cobalt carbonate and the carbonate, oxide, hydroxide, or nitrite of the other metal, in aqueous solution, with a current of nitrous anhydride, prepared from arsenic trioxide and nitric acid, until the cobalt carbonate is completely dissolved. The potassium salt, $3K_2O, Co_2O_3, 6N_2O_3$, and the rubidium and caesium salts are pure, deep yellow. The potassium salt, when boiled with water, dissolves with evolution of nitric acid, and the solution, on evaporation, yields a mixture of red and yellowish-brown crystals, which cannot be separated. The sodium salt, with xH_2O , prepared as described above, is precipitated from its aqueous solution by the addition of alcohol, as a microcrystalline, pure yellow powder, and does not contain water of crystallisation. Kahlbaum's "Natriumkobaltidnitrit" consists of this salt crystallising with $5\frac{1}{2}H_2O$. Both salts dissolve easily in water to a deep, yellowish-brown solution, which decomposes when heated. When the aqueous solution is treated with a potassium salt, a characteristic, yellow precipitate of the corresponding potassium salt is at once formed; similar precipitates are obtained with ammonium, barium, and lead salts, but with silver nitrate the characteristic precipitate of silver nitrite is obtained. The ammonium salt, with $1\frac{1}{2}H_2O$, crystallises in bright yellow rosettes, is slightly soluble in water, decomposes when the solution is warmed, and is very stable when dry. The barium salt, with $14H_2O$, is obtained by treating a mixture of cobalt carbonate and barium nitrite with nitrous acid; a deep brownish-red solution is obtained, which is filtered before all the cobalt carbonate is dissolved, and the filtrate is again treated with nitrous acid; it is a yellow, crystalline powder

consisting of microscopic six-sided tablets, is insoluble in water, is not so stable as the alkali salts, and is completely decomposed after remaining a few days. The *lead* salt, with $12\text{H}_2\text{O}$, obtained as a bright yellow powder by adding lead acetate to a solution of the sodium salt, and as a bright red, crystalline powder by treating a mixture of cobalt carbonate and lead oxide with nitrous acid, is very stable when dry, is insoluble in water, and, when treated with hydrogen sulphide, is completely decomposed.

Salt of the constitution $2\text{R}_2\text{O}, \text{Co}_2\text{O}_3, 4\text{N}_2\text{O}_3$.—The *sodium* salt is obtained by allowing the brown mother liquors obtained in the preparation of the above salt to evaporate over sulphuric acid; a reddish-brown, crystalline powder is obtained, which is not, however, the pure salt; when dissolved in water, it is not precipitated by alcohol; with nitrous acid, it yields the preceding salt; with potassium chloride, it does not give a precipitate, and when the mixture is allowed to evaporate over sulphuric acid, the corresponding potassium salt is obtained as a brown, microcrystalline powder. The *barium* salt, $2\text{BaO}, \text{Co}_2\text{O}_3, 4\text{N}_2\text{O}_3 + 10\text{H}_2\text{O}$, is obtained by allowing the deep red solution which is formed in the preparation of the preceding barium salt to evaporate over sulphuric acid; it crystallises in dark red crystals mixed with the yellow barium salt, barium nitrite, or cobalt nitrate, and has not yet been obtained in a pure state. The *strontium* salt, with $11\text{H}_2\text{O}$, is obtained by treating a mixture of cobalt carbonate (1 mol.) and strontium carbonate (1 mol.) with nitrous acid until a clear solution is obtained; when this solution is allowed to evaporate over sulphuric acid, it separates in small, red crystals.

Salt of the composition $2\text{RO}, \text{Co}_2\text{O}_3, 3\text{N}_2\text{O}_3 + x\text{H}_2\text{O}$.—The *zinc* salt, with $11\text{H}_2\text{O}$, obtained by treating a mixture of cobalt carbonate and zinc oxide with nitrous acid, crystallises in deep red, almost black, monoclinic pyramids. When dissolved in dilute acetic acid and treated with potassium chloride, it yields a precipitate of the salt $3\text{K}_2\text{O}, \text{Co}_2\text{O}_3, 6\text{N}_2\text{O}_3$, and, with ammonium salts, the corresponding ammonium salt. When treated with silver nitrate in concentrated solution, it yields the salt $2\text{Ag}_2\text{O}, \text{Co}_2\text{O}_3, 3\text{N}_2\text{O}_3 + 3\text{H}_2\text{O}$, which is sparingly soluble in water, and, when boiled with water, decomposes, with the formation of silver nitrite. The *cobalt* salt, $2\text{CoO}, \text{Co}_2\text{O}_3, 3\text{N}_2\text{O}_3 + \text{Co}(\text{NO}_3)_2 + 14\text{H}_2\text{O}$, obtained by treating cobalt carbonate suspended in water with nitrous acid, and allowing the brown solution to evaporate at the ordinary temperature, forms small, black crystals, and, when treated with silver nitrate, yields the preceding silver salt.

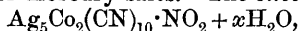
The authors were unable to obtain a cobaltmonammine nitrite by the reduction of the above salts; but they obtained diammine nitrites or triammine nitrites.

When potassium cobalt hexanitrite is warmed with potassium cyanide solution, it is converted into potassium cobalt cyanide, with evolution of gas.

The *sodium cobalt nitrocyanoide*, $\text{Na}_6\text{Co}_4(\text{CN})_{10} \cdot \text{NO}_2 + 11\text{H}_2\text{O}$, obtained by adding solid sodium cyanide to a well-cooled solution of the red salt, $\text{CoNa}_2(\text{NO}_2)_4 \cdot \text{OH}$, crystallises in microscopic needles, explodes

when heated, and gives off red, nitrous fumes when treated with acids. When potassium cyanide is employed instead of sodium cyanide, a green salt is obtained, mixed with cobalt potassium cyanide; this green salt, which cannot be obtained pure, explodes when heated, and is similar to the sodium salt.

Potassium cobalt nitrocyanide, $K_4Co_2(CN)_9 \cdot NO_2 + 3H_2O$, obtained by treating an ice-cold solution of the salt $K_4Co(CN)_6$ with nitrous acid, is precipitated by alcohol as a deep red oil, which usually solidifies after a time; it is stable when dry, but quickly decomposes in solution, and yields red precipitates of the corresponding salts when treated with silver, barium, lead, or mercury salts. The *silver salt*,



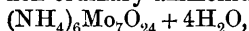
is a bright carmine red, amorphous powder, and is insoluble in water.

E. C. R.

Permolybdates. By WILHELM MUTHMANN and WILHELM NAGEL (*Zeit. anorg. Chem.*, 1898, 17, 73—81).—The authors have prepared the permolybdates as described by Bärwald (*Chem. Centr.*, 1885, 424), and Péchard (Abstr., 1891, 988; 1892, 1160, 1283, 1383) and find that these compounds have a different composition to that previously assigned to them.

The analysis of the salts is carried out as follows: the molybdenum is weighed as trioxide; in the case of ammonium salts this is obtained by heating the salt over a Bunsen burner; in the case of the other salts, the molybdenum is precipitated as sulphide, and this is then roasted. The oxygen is determined by titration with permanganate in acid solution, the permolybdic acid behaving with permanganate in the same way that hydrogen peroxide does; the ammonia is distilled and titrated, and the potassium weighed either as chloride or sulphate.

Ammonium salts.—When ordinary ammonium molybdate,



is dissolved in a carefully purified 20 per cent. solution of hydrogen peroxide, an orange-red and a lemon-yellow salt are formed. The *orange-red* salt, $3(NH_4)_2O \cdot 7MoO_4 + 12H_2O$, is obtained by allowing the saturated hydrogen peroxide solution to crystallise for 2 hours over phosphoric anhydride; it separates in beautiful, monoclinic crystals. The *lemon-yellow* salt, $3(NH_4)_2O \cdot 5MoO_3 \cdot 2MoO_4 + 6H_2O$, crystallises when the mother liquors of the preceding salt are concentrated further.

Potassium permolybdate, $K_2O \cdot 2MoO_3 \cdot MoO_4 + 3H_2O$, is obtained by dissolving potassium trimolybdate, $K_2Mo_3O_{10} + 3H_2O$, in hydrogen peroxide solution, and after separating a small quantity of amorphous precipitate, allowing the solution to evaporate over phosphoric anhydride, and then adding small crystals of the ammonium salt in order to start the crystallisation; it crystallises in minute, lustrous, bright yellow crystals belonging to the monoclinic system.

The assumption that hydrogen peroxide is present as such in these salts is supported by their behaviour towards potassium permanganate, also with chromic acid in sulphuric acid solution they give the blue coloration of perchromic acid, which is, however, quickly reduced; with a very dilute solution of potassium dichromate, aniline, and

oxalic acid, they yield the reddish-violet coloration characteristic of hydrogen peroxide; and they are extremely sensitive to alkali, a few drops of potassium hydroxide or ammonia being sufficient to decolorise them with a brisk evolution of oxygen. Against the assumption of the presence of hydrogen peroxide is the yellow colour of the salts; and the fact that the finely powdered ammonium salt, after remaining in a vacuum over phosphoric anhydride for three weeks, contained molybdenum and oxygen in the same ratio as when freshly prepared, although the ammonia and water were given off.

When heated, the orange ammonium salt decomposes at 105° , the yellow salt at 170° , and the potassium salt at 180° . When treated with sodium phosphate in dilute nitric acid solution, they do not give a precipitate; in concentrated solutions, the orange ammonium salt also gives no precipitate, but the yellow salt yields a precipitate varying from 30—40 per cent. of the molybdic acid, according to the concentration. When an aqueous solution of the orange ammonium salt is subjected to electrolysis, oxygen is evolved at the anode, and hydrogen at the cathode, whereby reduction and decolorisation take place, and finally lower oxides of molybdenum are deposited.

The above results are similar to those obtained by Piccini (Abstr., 1892, 784) by the action of hydrogen peroxide on fluoroxymolybdates whereby fluoroxypermolybdates are formed.

E. C. R.

Action of Hydrogen Sulphide on Vanadates. By JAMES LOCKE (*Amer. Chem. J.*, 1898, 20, 373—376).—When sodium orthovanadate is heated to 500 — 700° in a current of hydrogen sulphide, the latter is absorbed vigorously with production of sodium trithioorthovanadate, Na_3VOS_3 . Sodium pyrovanadate reacts in a similar manner, giving rise to *sodium pentathioypyrovanadate*, $\text{Na}_4\text{V}_2\text{O}_2\text{S}_5$, which, in the crystalline condition, resembles potassium permanganate in colour and lustre; when the hot salt is exposed to the air, it catches fire, gives off sulphurous anhydride, and is converted into sodium hypovanadate. The salt is very hygroscopic, and dissolves in water, to form a deep reddish-purple solution, rapidly changing in colour as hydrogen sulphide is given off, and finally becoming colourless. This colour change is accompanied by a remarkable alteration in the colour of the free thiovanadic acid, which separates on addition of hydrochloric acid. From the freshly prepared solution, the precipitate is black, and from the nearly oxidised solution is pale orange. These acids are, however, so unstable as to render their isolation in a pure state practically impossible.

In conjunction with J. S. North, the author has tried to prepare the thiovanadates of several of the heavy metals by this method. Lead vanadate alone yielded what seemed to be a definite compound in the form of a black, lustrous, crystalline powder of the probable composition $\text{Pb}_2\text{V}_2\text{O}_5\text{S}_2$.

A. W. C.

Sulphides. By VL. STANEK (*Zeit. anorg. Chem.*, 1898, 17, 117—125).—Silver sulphide (0.1 gram) when heated in a sealed tube with colourless ammonium sulphide (50 c.c.) for 4 hours at 150 — 200° , is obtained in beautiful, lustrous, black crystals, but when a relatively

larger amount of silver sulphide is employed, only indefinite crystals and crystalline incrustations are found. Thallium sulphide, treated in the same manner, is obtained in black, thin, six-sided plates and needles. Copper sulphide is obtained after prolonged action of the ammonium sulphide in thin, violet, six-sided leaflets. Cadmium and zinc sulphides are converted into crystalline powders. Cobalt, nickel, iron, bismuth, and lead sulphides remain unaltered even after 8 hours heating at 200° .

Two *ammonium thioantimonites* are obtained by the action of colourless ammonium sulphide on roughly powdered antimonite. The *compound* $\text{NH}_4\text{SbS}_2 + 2\text{H}_2\text{O}$, which is obtained at lower temperatures, crystallises in yellow, thin, four-sided needles or leaflets, has a violet fluorescence, and is insoluble in water; it decomposes on exposure to air, is insoluble in water, and when gently warmed loses part of the ammonium sulphide and all its water, and turns red without any alteration in crystalline form; when heated at 105° , it is converted into the following compound. It is decomposed by dilute acids, with the formation of antimony sulphide and hydrogen sulphide, and by potassium hydroxide with evolution of ammonia. The corresponding *potassium* salt separates in red crystals, and is soluble in water. The *compound*, $(\text{NH}_4)_2\text{Sb}_4\text{S}_7$, obtained by heating orange-red antimony sulphide or powdered antimonite with ammonium sulphide in a sealed tube at 150° , crystallises in beautiful, red needles, is stable on exposure to air, is not decomposed by heating at 200° , and at higher temperatures is decomposed into antimony sulphide and ammonium sulphide; it is insoluble in boiling water, and behaves like the preceding salt with acids and alkalis. The corresponding *potassium* salt separates in red crystals, with $3\text{H}_2\text{O}$, which turn brown and then black on exposure to light.

Ammonium thioantimonate, $(\text{NH}_4)_3\text{SbS}_4$, obtained by dissolving powdered antimonite and flowers of sulphur in red ammonium sulphide and recrystallising the product from colourless ammonium sulphide, crystallises in pale yellow prisms, which, after removal of the mother liquor, quickly decompose and become brown, and are easily soluble in water; it is decomposed by dilute acids, with formation of antimony pentasulphide and hydrogen sulphide, and when heated in carbonic anhydride yields ammonium sulphide, sulphur, and antimony trisulphide. When heated with antimony pentasulphide in a sealed tube at 150° , it is converted into the compound $(\text{NH}_4)_2\text{Sb}_4\text{S}_7$. It is obtained crystallising, with $4\text{H}_2\text{O}$, in aggregates of colourless needles by saturating colourless ammonium sulphide with antimony pentasulphide, adding an equal quantity of ammonium sulphide and then alcohol until a precipitate commences to form; the filtered solution is then covered with a layer of alcohol and allowed to remain.

Ammonium thiostannate, $(\text{NH}_4)_2\text{SnS}_3 + 3\text{H}_2\text{O}$, is obtained by saturating colourless ammonium sulphide with stannic sulphide, adding an equal quantity of ammonium sulphide, and then precipitating with alcohol; it crystallises in thin, yellowish tablets which quickly turn yellow on exposure to air, yields a slightly turbid solution with water which gradually deposits tin sulphide, and is decomposed by acids with

the formation of stannic sulphide and hydrogen sulphide. It is obtained with $7\text{H}_2\text{O}$, crystallising in beautiful, long, nacreous needles by covering a clear solution with a layer of alcohol and allowing the mixture to remain for some time. The *potassium* salt, K_2SnS_3 , is formed by boiling tin and sulphur with potassium sulphide; on adding alcohol to the solution, the salt is obtained as a yellow or brown oil with $9\text{--}10\text{H}_2\text{O}$. E. C. R.

Bismuthous Oxide. I. By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1898, 31, 1113—1118).—The substance obtained by fusing bismuth in contact with air is not bismuthous oxide, but a mixture of the ordinary oxide with the metal. When a solution of bismuth nitrate or oxychloride is treated with excess of stannous chloride and a large excess of 10 per cent. aqueous soda is added, the precipitate is not bismuthous oxide, but bismuth itself; the small amount of tin which it contains can be removed by washing with cold, dilute hydrochloric acid. The precipitate obtained by using only 1 mol. of stannous chloride, instead of 3, for every 2 atoms of bismuth present has been described as bismuthous oxide, but it is probably a mixture of the metal with the metahydrate. C. F. B.

Isomorphism between Salts of Bismuth and of the Rare Earths. By GÖSTE BODMAN (*Ber.*, 1898, 31, 1237—1240).—Just as thallium salts are isomorphous with those of potassium, rubidium, and caesium, it is to be expected that salts of bismuth are related in this way to those of scandium, yttrium, and lanthanum. The author shows that a solution containing bismuth and neodymium nitrates yields mixed crystals of varying specific gravity and composition; the two salts in question exhibit isodimorphism, the stable $\text{Bi}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$ yielding mixed crystals with the unstable salt, $\text{Di}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$, whilst the stable $\text{Di}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$ unites in a similar manner with unstable $\text{Bi}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$.

The analogous relationship between bismuth nitrate and the nitrates of lanthanum and yttrium has been also established. M. O. F.

Mineralogical Chemistry.

Heavy Liquid for Separating Minerals. By WILHELM MUTHMANN (*Zeits. Kryst. Min.*, 1898, 30, 73—74).—Acetylene-tetrabromide, $\text{CHBr}_2 \cdot \text{CHBr}_2$, which may be easily prepared by passing acetylene into bromine, has sp. gr. = 3.0011 at 6°, and refractive index = 1.6479 for sodium light. It is stable, and does not act on metallic minerals, and is miscible in all proportions with ether, benzene,

toluene, &c. It has the advantage of not darkening by exposure to light, and in being less than one-tenth the cost of methylenic iodide (sp. gr. = 3.35). The high refractive index also renders it available for optical purposes in place of monobromonaphthalene. L. J. S.

Stanniferous Argyrodite from Bolivia; Identity of "Crystallised Brongniardite" with Argyrodite. By GEORGE T. PRIOR and LEONARD J. SPENCER (*Min. Mag.*, 1898, 12, 5—14).—The cubic minerals argyrodite and canfieldite, which contain the rare element germanium, have already been noted from Bolivia by Penfield (*Abstr.*, 1894, ii, 18, 458). The canfieldite actually analysed by him contained the canfieldite and argyrodite molecules in the proportion of 12 : 5, namely, $12(4\text{Ag}_2\text{S}, \text{SnS}_2) + 5(4\text{Ag}_2\text{S}, \text{GeS}_2)$, whilst in the Bolivian, as well as in the original Freiberg, argyrodite no tin is present.

The material now described contains these two isomorphous molecules in different proportions, and is nearer to argyrodite than to canfieldite. It comes from Aullagas, dept. Potosi, and is associated with pyrargyrite, together with a little stephanite, blende, pyrites, barytes, and kaolin. Two types of the very symmetrically developed crystals are distinguished: (1) simple untwinned octahedra, usually with narrow dodecahedral planes, $d\{110\}$, and (2) dodecahedral crystals always twinned, and never with octahedral planes. The mineral is iron-black, with a dull, metallic lustre; the fracture is even, with a finely granular appearance. Analysis by G. T. Prior gave,

Ag.	Ge.	Sn.	S.	Fe.	Sb.	Total.	Sp. gr.
74.20	4.99	3.36	16.45	0.68	trace	99.68	6.19

The trace of antimony is due to the presence of pyrargyrite. Formula, $5(4\text{Ag}_2\text{S}, \text{GeS}_2) + 2(4\text{Ag}_2\text{S}, \text{SnS}_2)$. A convenient method for detecting germanium is to heat the mineral in a current of hydrogen, when there is a deep reddish-brown and black sublimate of germanium disulphide and metallic germanium formed on the sides of the tube; this is dissolved off by nitric acid, and from the solution of the sulphide in ammonium sulphide, the bulky, pure white germanium bisulphide is precipitated on adding a large excess of sulphuric acid.

Brongniardite was described by Damour, in 1849, as a massive mineral from Bolivia having the composition $\text{PbS}, \text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$. Five years later, he described cubic crystals, which, from a blowpipe examination, he stated to be crystals of brongniardite. A re-examination of these crystals, from Aullagas, shows that they contain germanium, tin, and about 72 per cent. of silver, and that they are identical in all their characters with the argyrodite described above.

The sulphostannates at present known to occur as minerals are—canfieldite, stannite, franckeite, kylindrite (*Abstr.*, 1893, ii, 576), and plumbostannite, all of which, with the exception of stannite, occur only in the Bolivian region. As pointed out by Stelzner (this vol., ii, 121), the Bolivian silver-tin veins are of an exceptional character, and it is just under these conditions that sulphostannates would be likely to be found. L. J. S.

Gypsum in Kansas. By GEORGE P. GRIMSLEY (*Jahrb. f. Min.*, 1898, i, Ref., 259—260; *Kansas Univ. Quart.*, 1897, 6, A, 15—27; and *Bull. Geol. Soc. Amer.*, 1897, 8, 227—240. Compare Abstr., 1897, ii, 415).—The extensive gypsum deposits occurring in the Permian rocks of Kansas are described. The following varieties are found: granular gypsum rock; large crystals; satin spar; and “dirt”; the last is an earthy powder of dark colour, and consists of small crystals of gypsum and quartz, with some calcite, and traces of organic matter. The massive gypsum was deposited in gulfs of the Permian seas, whilst the “dirt” is a recent deposit from springs. Analyses are given of: I, Gypsum rock from Hope; II, white gypsum from Medicine Lodge; III, “dirt” from Dillon; IV, “dirt” from Longford.

	SiO ₂ .	Fe ₂ O ₃ .	CaSO ₄ .	CaCO ₃ .	MgCO ₃ .	H ₂ O.	Total.
I.	0·34	0·16	76·98	1·68	1·38	19·63	100·17
II.	0·19	0·10	77·46	1·43	0·34	20·48	100·00
III.	12·13	0·99	64·63	3·57	0·88	16·80	99·00
IV.	18·69	1·21	56·56	6·10	0·90	15·54	99·00

L. J. S.

Kubeite. By L. DARAPSKY (*Jahrb. f. Min.*, 1898, i, 163).—This name is given to deep red crystals from near the river Loa, in the desert of Atacama; they are orthorhombic or monosymmetric pyramids, with a vitreous lustre, and are very brittle. Analysis gave,

SO ₃ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	MgO.	CaO.	Insol.	H ₂ O.	Total.
36·4	19·3	Nil.	7·8	[0·1]	2·7	33·7	100·0

This agrees approximately with the formula $2(\text{Fe}_2\text{O}_3, 2\text{SO}_3) + 3(\text{MgO}, \text{SO}_3) + 30\text{H}_2\text{O}$, and is analogous to the magnesia alum common on the coast of Chili.

L. J. S.

The Occurrence and Extraction of Thorite, Monazite, and Zircon. By P. TRUCHOT (*Chem. News*, 1898, 77, 145—147).—*Monazite*.—This mineral occurs at Cleveland, North Carolina, in crystals, only slightly decomposed, and disseminated in coarse mica (both muscovite and biotite); the ground is also rich in thoria; it is worked to a depth of 1·2 to 1·8 metre and is sluiced. In Idaho, monazite occurs as a constituent of granite and also in sands associated with zircon, ilmenite, &c., or with rutile, garnet, &c. In Ottawa Co., Canada, it is associated with mica, garnet, tourmaline, &c. Large supplies, too, are drawn from sandbanks on the sea shore of Bahia province, Brazil; these sands contain a notable proportion of monazite and 4 to 5 per cent. of thoria, and are directly loaded on board ship; in Brazil, it is also found, in nodular masses, coloured by orangite, in the gold and diamond placers in the provinces of Minas Geraes, Cuyaba, and Goyaz, also in the provinces of San Paulo and Rio de Janeiro. Other localities are Antioquia, New Granada; the United States of Columbia; the sands of the Buenos Ayres river in the Argentine Republic, &c. In the following table, the average composition of monazite and monazite sands from different localities is given.

	Monazite.	P ₂ O ₅ .	Ce ₂ O ₃ .	La ₂ O ₃ .	Di ₂ O ₃ .	Yt ₂ O ₃ .	ThO ₂ .	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	
I. Mount Ilmen ...	{	27·32	31·31	31·86	—	0·52	5·55	1·37	0·13	0·26	
II. Antioquia.....		19·31	22·88	14·69	—	1·71	16·64	9·67	2·90	—	
		29·10	46·14	24·50	—	—	—	—	—	—	
III. Caravellas, Brazil	{	28·70	31·30	39·90		—	—	—	—	—	
IV. Burke Co., N. Carolina		29·23	31·38	30·88		—	6·49	1·40	—	—	
V. Amelia Co., Virginia	{	26·12	29·89	26·66		—	14·23	2·85	—	—	
VI. Ottawa Co., Canada		26·86	24·84	26·41		4·76	12·60	0·91	—	1·07	
Monazite sands.											
VII. Burke Co., N. Carolina	{	18·38	32·93(CeO) 7·93			—	1·43	6·40	1·62	—	
VIII. Shelby, N. Carolina		28·16	63·80			—	2·32	3·20	—	—	
IX. Bellewood, N. Carolina	{	26·05	59·09			—	1·19	1·45	0·15	—	
		FeO.	MnO.	CaO.	MgO.	ZrO ₂ .	SnO ₂ .	PbO.	Ta ₂ O ₅ .	TiO ₂ .	H ₂ O.
I. {	—	—	0·55	—	—	0·95	—	—	—	—	0·41
II. {	3·56	4·89	1·25	0·40	—	0·40	—	—	—	—	0·71
III. —	—	—	—	—	—	—	—	—	—	—	—
IV. —	—	—	—	—	—	—	—	—	—	—	0·20
V. —	—	—	—	—	—	—	—	—	—	—	0·67
VI. —	—	—	1·54	0·04	—	—	—	—	—	—	0·78
VII. —	7·83	—	1·20	—	13·98*	—	traces	0·66	4·67	—	—
VIII. —	—	traces	—	—	1·52*	—	—	—	0·61	—	—
IX. —	0·65		—	—	2·68*	—	—	6·39	1·40	—	—
* + Y ₂ O ₃ .											

* + Y₂O₃.

Zircon.—Well known localities of occurrence are duly recorded, and, in addition, certain recent discoveries in North Carolina, Colorado, Idaho, and Texas, where zircon is associated with monazite. The largest deposit, 105 acres in extent, is situated to the north-east of Tasmania, 20 to 30 cm. below the surface, in a gravel bed 20 cm. thick, which rests on a bed of blue clay 60 cm. thick. The deposit consists almost entirely of zircon with variable quantities of lanthanum, didymium, thorium, niobium, erbium, cerium, and chromium. The average composition of zircons is as follows.

	Ceylon.	Norway.	Colorado.	New Zealand.
SiO ₂	33·85	33·61	29·70	33·50
ZrO ₂	64·25	64·40	60·98	63·80
FeO	1·08	0·90	9·20	2·07
MgO	—	—	0·30	0·12

D. A. L.

Artificial Scorodite. By HERMANN METZKE (*Jahrb. f. Min.*, 1898, i, 169—170).—By heating various ferric arsenates with an aqueous solution of arsenic acid in sealed tubes, crystalline precipitates were obtained having approximately the composition of scorodite (FeAsO₄ + 2H₂O). In one experiment (in the presence of hydrogen

peroxide) distinct crystals of scorodite were produced, together with orthorhombic crystals having perhaps the composition $2\text{FeAsO}_4 + \text{H}_2\text{O}$. Crystalline material was also obtained by the evaporation of a hydrochloric acid solution of ferric arsenate.

L. J. S.

Position of Bliabergite in the Mineral System. By MATS WEIBULL (*Jahrb. f. Min.*, 1898, i, Ref., 246—247; from *Geol. För. i Stockholm Förh.*, 1896, 18, 515).—A re-examination of the mineral recently described by Igelström under the name bliabergite or bliabergsite (Abstr., 1897, ii, 268), shows it to be a brittle mica near chloritoid or ottrelite. It occurs as rounded, rarely hexagonal, plates, which, when fresh are greyish-green, and have a hardness = 7, sp. gr. = 3.6. There is a distinct cleavage in one direction. Optical examination shows it to be monosymmetric, strongly pleochroic, and to enclose much hæmatite, kyanite, quartz, and limonite. Owing to these impurities, the analyses are unsatisfactory (compare Barrow, this vol., ii, 389). The iron ores were dissolved by hydrochloric acid, and the quartz separated by a heavy solution, but the material so obtained still contained 15—20 per cent. of kyanite; the portion of this soluble in sulphuric and hydrofluoric acids gave I, which is taken to represent the composition of the bliabergite. Analysis of purer material gave II, after deducting 20 per cent. of kyanite.

	SiO_2 .	Al_2O_3 .	FeO, MnO .	MgO .	H_2O .
I.	37.59	25.50	29.31	0.65	6.97
II.	40.07	32.39	21.06	1.20	4.06

A structural formula is given. Bäckström, from an optical examination, also concludes that bliabergite is an altered ottrelite.

L. J. S.

Sphærostilbite. By GEORGE T. PRIOR (*Min. Mag.*, 1898, 12, 26—29).—It is shown that the material called sphærostilbite, from the Farøe Islands, and other localities, has the optical characters and the chemical composition of thomsonite and not of stilbite. Material from the Farøe Islands consists of a sort of open network of confusedly-grouped and imperfect crystals, presenting pearly cleavage surfaces, and resembling stilbite, disposed on ordinary compact mesole (farøelite), the presence of which determines the spherical form. Both of these portions have the optical characters of thomsonite; and material from the outer zone carefully separated from the more compact spheres of mesole, gave the following results on analysis.

SiO_2 .	Al_2O_3 .	CaO .	Na_2O .	H_2O .	Total.
40.69	28.63	12.98	5.66	12.42	100.38
41.47	28.69			12.63	

In all probability, the sphærostilbite originally described by Beudant in 1832 does not exist, and that described by Heddle is probably identical with the material now shown to be thomsonite; the name sphærostilbite must therefore be discarded.

L. J. S.

Senaite, A New Mineral of the Ilmenite Group, from Brazil. By EUGEN HUSSAK and GEORGE T. PRIOR (*Min. Mag.*, 1898, 12, 30—32).—This new ilmenite-like mineral occurs as rounded fragments and

rough crystals in the diamond-bearing sands of Diamantina in Minas Geraes. The crystal system is rhombohedral, tetartohedral (trigonal rhombohedral of Groth); $a:c=1:0.997$. The crystals are very rich in faces and are frequently twinned. The colour is black, with sub-metallic lustre, and the powdered mineral is brownish-black; very thin splinters are transparent with an oil-green to greenish-brown colour. There is no cleavage, and the fracture is conchoidal. The sp. gr. of crystals is given as $=4.22, 5.08$ and 5.301 , these differences being apparently due to decomposition, as the crystals are sometimes coated with brown limonite, or with a yellow crust consisting of titanite acid with only a trace of iron. The mineral is infusible before the blowpipe, and is decomposed by hydrofluoric acid, by boiling sulphuric acid, and by fusion with acid potassium sulphate. Analysis by G. T. Prior of the rounded fragments of sp. gr. $=4.78$, and apparently quite fresh and homogeneous, gave

TiO ₂ .	PbO.	FeO.	Fe ₂ O ₃ .	MnO.	MgO.	SnO ₂ .	Total.
57.21	10.51	4.14	20.22	7.00	0.49	0.11	99.68

Considering all the iron to be FeO, and the manganese MnO₂, the formula is approximately (Fe,Pb)O,2(Ti,Mn)O₂. The amount of titanite acid is much too great for the ordinary ilmenite formula, FeO,TiO₂, advocated by Penfield and Foote (this vol., ii, 122). Other analyses of ilmenite showing the same excess of titanite acid are those by Mackintosh (Abstr., 1885, 878) and Peek (Abstr., 1897, ii, 328); and of Janovsky's iserite the formula is FeO,2TiO₂.

L. J. S.

Chemical Constitution of the Chlorite Group. By K. DALMER (*Jahrb. f. Min.*, 1898, i, Ref. 165—168).—Tschermak has assumed the chlorites to be mixtures in various proportions of silicates having the composition of serpentine, amesite, &c. The fundamental molecules assumed by the present author are chloritoid and olivine. L. J. S.

So-called Hornblende-gneisses in Moravia. By CONRAD H. VON JOHN (*Jahrb. f. Min.*, 1898, i, Ref. 279; from *Verh. geol. Reichsanst.*, 1897, 189—193).—Several so-called hornblende-gneisses from various localities in Moravia are shown to have a mineralogical composition and structure between syenite and diorite, and they may therefore be called monzonite (of Brögger). Plagioclase felspar is slightly more abundant than orthoclase, both hornblende and biotite are present, and there is very little quartz. Analysis I, of the rock from Chudoba, Bohemia; II, from Hackelsdorf, Moravia.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	P ₂ O ₅ .	Loss on ignition.	Total.
I. 57.79	17.58	1.79	5.32	5.80	3.85	3.11	3.43	0.49	0.66	99.82	
II. 58.18	17.00	2.02	5.20	5.90	3.93	2.96	3.40	0.32	0.74	99.65	

L. J. S.

Meteoric Iron from Ballinoo, Western Australia. By EMIL W. COHEN (*Ber. Akad. Berlin*, 1898, 19—22. Compare this vol., ii, 342).—As before mentioned, this is an octahedral iron consisting

mainly of plessite with very fine lamellæ of kamacite and ténite. Analysis by O. Sjöström gave,

Fe.	Ni.	Co.	Cu.	C.	P.	S.	Total.	Sp. gr.
89·34	9·87	0·60	0·06	0·02	0·48	0·03	100·40	7·8432

This corresponds with the mineralogical composition: nickel iron, 96·81; schreibersite, 3·11; and troilite, 0·08 per cent. L. J. S.

Composition of the Atlantic Ocean. By CHARLES J. S. MAKIN (*Chem. News*, 1898, 77, 155—156, 171—172).—Samples of water from the Atlantic Ocean were taken daily at noon, during a homeward voyage from the Cape; there were twenty-two samples in all. The total solids were determined in each sample, and varied from 34·51 per 1000 (taken during a continued heavy rain) to 37·39 per 1000 (taken at Teneriffe, 200 yards from shore, in about 11 fathoms). The samples were mixed, and a full analysis made of the average sample so obtained; it had a sp. gr. = 1·0275 at 15·5°, and contained, in parts per 1000: Total solids, 36·31; Cl, 20·6569; Br, 0·0671; CO₂, combined, 58·46; CO₂, free, 5·11; SO₃, 24·679; CaO, 0·6518 (vol.); MgO, 2·4270; Na₂O, 1·5266; K₂O, 0·049952. Ammonia (milligrams per litre), free, 0·192; combined, 0·362; albuminoid, 0·558; organic matter, equal to 10·40 and 11·00 milligrams of oxygen per litre. The various methods of analysis employed are recorded. D. A. L.

Physiological Chemistry.

Fat Absorption. By OTTO FRANK (*Zeit. Biol.*, 1898, 36, 568—593).—Ethylic salts of the higher fatty acids are (with the exception of the stearate) taken up in large quantities from the dog's alimentary canal. Before absorption, they are completely broken up in the small intestine, so that not the smallest quantity appears in the chyle. It is quite certain that, in the absorption of fat, there is a synthesis of triglycerides from fatty acids and glycerol. In the chyle, some of the fat originates from the intestine and its juices. W. D. H.

The Formation of Urea in the Liver of Mammalia from Amido-acids of the Fatty Series. By SERGEI SALASKIN (*Zeit. physiol. Chem.*, 1898, 25, 128—151).—By means of experiments on dogs, similar in principle to those by means of which Schröder established the fact that ammonium salts are transformed in the liver into urea, it is shown that the liver can form urea also from the amido-acids, glycocine, leucine, and aspartic acid. Whether other nitrogenous compounds, such as proteoses, peptone, carnic acid, &c., act similarly, has yet to be tested. W. D. H.

Variations in the Activity and Composition of Human Mixed Saliva. By RUSSELL H. CHITTENDEN and A. N. RICHARDS (*Amer. J. Physiol.*, 1898, 1, 461—476).—A full account of experiments previously published (see this vol., ii, 241). W. D. H.

The Contents of Occluded Portions of the Intestine. By WACŁAW VON MORACZEWSKI (*Zeit. physiol. Chem.*, 1898, 25, 122—127).—In a dog, the ileum, cæcum and commencement of the colon were ligatured off from the rest of the alimentary canal; the continuity of the rest of the canal was then restored, the animal recovered well, and was killed a year later. The ligatured intestine presented the appearance of a sac, the contents of which resembled meconium in appearance, and contained numerous bacteria (not *Bacterium coli*). Analysis showed 74 per cent. of water, and the solid residue yielded neutral fat, 10; cholesterol and stercorin, 6; pigment (dissolved out with amylic alcohol), 5; fatty acids, 27; proteid, 1; salts, 20; chlorides, 0.03 per cent.; 31 per cent. of the solids are left unaccounted for. The material is remarkable for its high percentage of salts. Sugar, enzymes, indole, lecithin were absent. The material had a scatole-like odour.

In another dog, a similar operation involved a part of the ascending colon. A year later, the sac contained an uncoloured, strongly alkaline liquid, with a scatole-like odour, and the appearance of a transudation. The contents of this were chiefly water and salts, especially sodium carbonate; there was a little proteid, but no sugar, fat, cholesterol, or lecithin.

On the strength of these two experiments, the conclusion is drawn that the small intestine secretes pigments, fat, and calcium salts; the large intestine, almost nothing else but sodium carbonate.

W. D. H.

Comparative Composition of Blood. By EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1898, 25, 65—115. Compare this vol., ii, 35, 415).—A large number of analyses of the blood of various oxen, sheep, goats, horses, pigs, rabbits, dogs, and cats are given in a series of tables.

W. D. H.

Intestinal Absorption and Saline Cathartics. By GEORGE B. WALLACE and ARTHUR R. CUSHNY (*Amer. J. Physiol.*, 1898, 1, 411—434).—The absorption of the salts of the fixed alkalis varies with the anions, those acids which form insoluble calcium salts tending to retard absorption more than others. The behaviour of these salts in the intestine has much in common with their action on unorganised colloid matter, as they tend to precipitate colloids in solution, and are less imbibed than other salts by undissolved colloids. But no complete analogy in their behaviour towards the tissues in general exists, for several of the cathartic salts permeate the red corpuscles freely, and others are absorbed rapidly from the serous membranes.

As regards the cations, ammonium is absorbed more rapidly than the fixed alkali ions, whilst those of the alkaline earths are very slowly taken up by the intestinal epithelium.

Dilute solutions (isotonic) of the saline cathartics retard the absorption of fluid from the stomach and small intestine, and thus act by rendering the contents more watery, and more easily moved through the lower parts of the alimentary canal.

W. D. H.

Secretion of Acids by Molluscs. By K. SCHOENLEIN (*Zeit. Biol.*, 1898, 36, 523—548).—It is well known that *Dolium galea* and other

snails secrete from the glands at the anterior end of their alimentary canal a liquid rich in sulphuric acid (3 to 4 per cent.). Opportunity was afforded the author of obtaining a few specimens of these animals at Naples, and he confirms the observation. Microscopical examination of the glands shows that they resemble the submaxillary gland very much. It is not so generally known that the number of molluscs with similar acid secretions is very great. A list of these is given. In one case (*Pleurobranchidium meckelii*), the secretion of the skin is acid. In another case (*Tritonium*), which was more fully investigated, the secretion was acid, and contained proteid material. The acid is an organic, crystallisable, nitrogen-containing substance, which was not, however, identified.

The formation of gas-bubbles, so characteristic a feature of *Dolium*, is due to the action of the sulphuric acid on concretions of calcium carbonate.

The dissection of the glands, and the obtaining of the secretion in these large molluscs, is a matter of some difficulty; the shell is hard, and muscular tonus after a wound intense; this was to some extent overcome by keeping the animals at 30°, and injecting pelletierin.

W. D. H.

Noël-Paton's Crystalline Globulin. By KARL H. HUPPERT (*Centr. med. Wiss.*, 1898, No. 28).—The crystalline proteid described by Noël-Paton (*Abstr.*, 1893, ii, 290) in a specimen of human urine, was regarded by Huppert (*Abstr.*, 1897, ii, 221) as probably heteroalbumose. He has now had an opportunity of examining the actual material, and fully confirms Paton's statement that it is a globulin.

W. D. H.

Urine of Octopus Macropus. By K. SCHOENLEIN (*Zeit. Biol.*, 1898, 36, 548).—This secretion is clear, colourless, and slightly acid; the cause of the acidity is still to seek. The acidity increases on evaporation. The urine contains a considerable amount of sodium chloride. There is also a deposit like sand, which consists of orange-red, globulo-crystalline concretions; these give the murexide reaction.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

A New Organism, the *Bacillus Tartricus*, capable of Fermenting Tartrates. By LÉON GRIMBERT and L. FICQUET (*J. Pharm.*, 1898, [vi], 7, 97—100).—Hitherto the fermentation of tartrates has only been studied in the case of impure cultures. By exposing a few drops of a vegetable infusion to the air at 35°, and making a series of anærobic cultures of the organisms developed, in solutions of tartrate and of gelatin, the authors have isolated a probably new organism, the *Bacillus tartricus*, which rapidly ferments calcium tartrate, converts

nitrites, and decomposes dextrose, lactose, maltose, cane-sugar, dextrin, and mannitol, but does not act on dulcitol or glycerol. No alcohol was formed on fermenting calcium tartrate at 36° with either aerobic or anaerobic cultures of the organism in presence of Pasteur's nutrient fluid and a trace of peptone; acetic and succinic acids, together with hydrogen and carbonic anhydride, were alone obtained. Ammonium tartrate, under the same conditions, gave rise to acetic and succinic acids only. By these properties, the *Bacillus tartricus* is distinguished from the organisms capable of fermenting tartrates, which have been described by Pasteur, Gautier, Fitz, and König.

W. A. D.

Nucleo-proteids of Bacteria. By GINO GALEOTTI (*Zeit. physiol. Chem.*, 1898, 25, 48—63).—The question of immunity, and of toxins and anti-toxins produced by bacteria, is closely linked with that of the chemical composition of the micro-organisms themselves. Several previous researches (references to which are given) indicate that the proteid material they contain is nucleo-proteid.

The bacterium specially investigated during the present research was Ernst's *Bacillus ranicidus* (*Zeigler's Beiträge*, 1890, 203), large cultures of which were obtainable. The nucleo-proteid separated from this by the usual methods yielded xanthine bases; it contained a low percentage of nitrogen (12), whilst the phosphorus amounted to 1.01 to 1.8 per cent. It produced intravascular coagulation in rabbits, but small doses conferred immunity. The concluding portion of the paper relates to its colour reactions with aniline dyes.

W. D. H.

Denitrifying Micro-organisms. By OTTO KÜNNEMANN (*Landw. Versuchs-Stat.*, 1898, 50, 65—113).—The destruction of nitrates by micro-organisms was first established by Meusel (this Journal, 1876, 189). Horse-dung contains two kinds of micro-organisms which destroy nitrates, one of which (Burri and Stutzer's *Bacillus denitrificans I.*) is effective only in symbiosis with *Bacterium coli*, the other (which was also found in straw) is a variety of *Bacillus denitrificans II.* (Burri and Stutzer). The same micro-organisms were found in cattle dung, but they are not always present.

The loss of nitrates caused by denitrification may be not inconsiderable, but is less in soil poor in organic matter. Both exclusion of air and abundant aëration retard the action of *B. denitrificans I.*, but have no effect on *B. denit. II.*

Sulphuric acid is very effective in preventing denitrification, the micro-organisms being unable to develop in solutions containing 0.17 per cent. of the acid.

A number of soils were next examined for denitrifying organisms which were generally found to be present. The varieties were, however, usually different from those found in dung. The denitrifying bacteria found were *Bacillus pyocyaneus*, *B. fluorescens liquefaciens*, and a third, not previously described, *B. denitrificans III.* The activity of these microbes is equal to those found in dung. Their growth is stopped by 0.17 per cent. of sulphuric acid.

Denitrification is not disturbed by 0.1 per cent. of caustic lime, but

is slower in presence of 0.25 per cent. With 0.5 per cent. of lime, *B. pyocyaneus* alone caused denitrification. Marl has no effect.

N. H. J. M.

Processes of Denitrification. By THEODOR PFEIFFER and OTTO LEMMERMANN (*Landw. Versuchs-Stat.*, 1898, 50, 115—142).—An extension of Künnemann's experiments (preceding abstract). The variety of *B. denitrificans* II. found in straw liberated 89.93 per cent. of the nitric nitrogen in a Giltay solution as free nitrogen. In Giltay and Aberson's experiments (*Extrait Arch. Néerland.*, 25, 341), about 80 per cent. of the nitric nitrogen was liberated, whilst Burri and Stutzer recovered 98.9—99.6 as free nitrogen. A certain amount of the nitrogen of the nitrates was converted into organic nitrogen. In broth, 95.52 per cent. of the nitric nitrogen was liberated. Both in a Giltay solution and in broth, a considerable amount of carbonic anhydride was liberated, and in broth cultivations a certain amount of hydrogen was produced. It is, however, most improbable that the production of nascent hydrogen is the direct cause of denitrification; such an action would not stop at the point at which nitrates are produced, and a greater amount of elementary nitrogen would be formed than corresponds with the original nitrate. Finally, no hydrogen was detected during denitrification in a Giltay solution.

The different denitrifying organisms were cultivated in nitrate broth in air, oxygen, hydrogen, and carbonic anhydride respectively. Hydrogen slightly retarded denitrification; the micro-organisms thrive without oxygen, but seem to require air when they commence to develop. The bacteria did not grow in pure carbonic anhydride. With regard to air and pure oxygen, *B. denit.* II. var. was rather benefited than restrained by abundant aëration, but the other varieties seem to be injured. Assuming the denitrifying organisms found by Künnemann in soil to be the only ones present, aëration of soil would, at any rate, not increase loss of nitrogen through denitrification (compare Ehrenberg, *Abstr.*, 1887, 172 and 746; 1888, 185).

With regard to the question of the injurious effect of fresh horse-dung, with and without nitrate, on the yield of crops (Wagner, *Landw. Versuchs-Stat.*, 48, 238), experiments are described in which oats were grown in pots containing 27 kilos. of sandy soil, to which sodium nitrate (7.41 grams) and horse-dung (500 grams), both alone and mixed, were added. Some of the pots had, in addition, caustic lime (15 and 25 grams) and marl respectively. The results were much less unfavourable than those obtained by Wagner (*loc. cit.*, and *Deut. landw. Presse*, 9 Feb., 1895), the effect of sodium nitrate being, in the worst case, depressed from 70.8 to 42.4 per cent. This difference is attributed to the fact that Wagner added 2 grams of nitrogen (in dung) to 7 kilos. of soil, whilst in these experiments only 1.7 grams of nitrogen was added to 27 kilos. of soil; in presence of the greater amount of organic matter, the micro-organisms are more active. In the authors' experiments the amount of dung applied corresponds with over 480 lbs. per acre; moreover, fresh dung is rarely used in practice, and the experiments cannot therefore be considered unduly favourable. The

actual loss, as free nitrogen, in practice is probably less important than is supposed, but further evidence is wanted.

Lime and marl slightly impeded denitrification, and the beneficial effect of the application of these substances to the soil is, in most cases, to be partly attributed to this action. N. H. J. M.

Two Moulds Capable of Producing Citric Acid. By CARL WEHMER (*Chem. Zeit.*, 1897, 21, 1022—1023).—It has been found that the mould, *Penicillium luteum*, which has been previously described by the author from a morphological point of view (*Ber. botan. Ges.*, 1893, 4), is capable of producing citric acid from saccharine solutions. The amount of acid formed is always small, never more than 2—3 per cent. The mould grows readily on strongly acid substrata, and may readily be obtained together with *Aspergillus niger* by spontaneous growth. A second mould which is also capable of forming citric acid is *Mucor piriformis*, Fisch.; the amount of acid formed by this organism is greater than that by *Penicillium luteum*, but with both organisms it has been found that occasionally no trace of citric acid is formed, even when all conditions are practically identical. The second organism, when grown on steamed rice, develops a characteristic ethereal odour.

Experiments made with *Citromyces pfefferianus* have established the absolute necessity for oxygen in order that the organism may grow and that citric acid may be formed. J. J. S.

Assimilation of Iron from Cereals. By GUSTAV VON BUNGE (*Zeit. physiol. Chem.*, 1898, 25, 36—47).—Analyses previously published of food materials have shown that, in comparison with rice, the cereals are very rich in iron. The greater quantity of this element is, however, in the husk or bran.

The author finds the amount of iron (in milligrams per 100 grams of dry substance) to be as follows.

Rice.....	1 to 2	Rye	4·9
Peeled barley	1·4 to 1·5	Wheat	5·5
Wheat meal	1·6	Wheat bran.....	8·8
Barley	4·5		

The question next arises whether the iron compound in the bran is assimilable, and experiments were made in parallel series on rats fed on bread, with and without bran respectively. It was found that the weight, the absolute quantity of hæmoglobin in the animal, and the amount of hæmoglobin per body weight were all increased in the case of those to which the bran was given to a greater extent than in the others. The conclusion is therefore drawn that the iron compound in the bran is assimilable and converted into hæmoglobin.

W. D. H.

Saps. II. By ALEXANDRE HÉBERT (*Bull. Soc. Chim.*, 1897, [iii], 17, 88—91. Compare Abstr., 1896, ii, 494).—The sap of the European banana tree (*Musa ensete*) is distinguished from that of the foreign variety (*Musa paradisiaca*), previously described, by the absence of

colouring matter and fatty acids, and by the presence of glucose. It is concluded that the processes of assimilation may differ considerably in different varieties of the same botanical species. N. L.

Mode of Formation of Elaterin in Ecballium Elaterium. By ARMAND BERG (*Bull. Soc. Chim.*, 1897, [iii], 17, 85—88).—When the fruit of *Ecballium elaterium* is cut up and pressed, a turbid liquid is obtained which deposits a pale green powder, of which the chief constituent is elaterin. If, however, the entire fruit is rapidly pressed, the liquid obtained is at first clear, but soon becomes clouded. This phenomenon is explained by the fact that elaterin does not exist ready formed in the fruit, but is produced, after the rupture of the tissues, by the action of a ferment on a glucoside. Both of these substances have been isolated from the clear juice. The examination of the ferment, for which the name *elaterase* is suggested, is not yet completed. The *glucoside* is a very bitter, amorphous, yellowish powder, slightly soluble in water, very soluble in alcohol, chloroform, and acetone, but insoluble in ether and benzene. With sulphuric acid and phenol, it gives the same reactions as elaterin. N. L.

The Nature of the Reducing Sugar in Sugar-cane Sap, Cane-sugar Molasses, and Sorghum Products. By C. H. PELLET (*Bied. Centr.*, 1898, 27, 357; from *Bul. inst. égypt.*, and *Neue Zeits. Zuckerind.*, 1897, 237, 245, and 261).—Levulose and dextrose are present in sugar-cane juice, but in varying amounts. In sugar-cane poor in sugar, containing much reducing sugar, there is more levulose than dextrose, whilst in rich canes containing little reducing sugar there is more dextrose. The upper portions of the canes are richer than the lower in reducing sugar and contain more levulose, and *vice versa*.

In determining the reducing sugar in sugar-cane juice, in order to estimate the amount of crystallisable sugar, the solution should be treated with lead solution which has been neutralised with acetic acid, otherwise a not inconsiderable amount of levulose is precipitated. In some cases, the raffinose must be determined. The reducing sugars from cane and from sugar-cane molasses ferment exactly in the same manner as invert-sugar, which they also resemble in their behaviour towards lime and alkalis.

In order to calculate the amounts of dextrose and levulose in sugar-cane juice (or the molasses), it is necessary to know (1) the difference between the direct polarisation and the actual crystallisable sugar determined by inversion ($-D$), and (2) the total amount of reducing substances (R), the rotatory power of levulose at the temperature at which the experiments were made, and the rotatory power of the dextrose. The levulose being x and its rotatory power L , the dextrose y and its rotatory power 0.793 : $0.973 y - L \times x = -D$ and $x + y = R$. The general formula is then $x = R - y$, $y = \frac{RL - D}{L + 0.793}$.

N. H. J. M.

Presence of Amygdalin and Emulsin in the Seeds of Certain Pomaceæ. By LUTZ (*Chem. Centr.*, 1897, ii, 1054; from *Rép. Pharm.*, 1897, 312).—The distillates obtained from the seeds of *Malus com-*

munis, *Cydonia vulgaris*, *Cydonia japonica*, and *Sorbus aria* contain hydrocyanic acid, and 0.032 gram of this acid is present in the seeds of *Sorbus aucuparia*. To test for emulsin, the cut surfaces of the seeds are moistened with Millon's reagent diluted with five times the volume of water acidified with nitric acid; the cells become rose-coloured, and, on warming, those which contain emulsin turn light brown.

E. W. W.

Iceland Moss. By ERNEST W. BROWN (*Amer. J. Physiol.*, 1898, 1, 455—460).—The bitter constituents of the lichen *Cetraria islandica* (Iceland moss) must be removed by treatment with water or weak alkali before it can be made into palatable bread. Its composition is as follows.

Total nitrogen	0.56 per cent.
Extractives	0.14 "
"Protein"	0.32 "
Ether extract (fat and fatty acids)	1.2 "
Crude fibre	5.3 "
Fat	2.2 "
Material soluble in 85 per cent. alcohol ...	16.1 "
Soluble carbohydrates (as dextrose)	43.3 "

The quantity of proteids is thus small and resists artificial digestion. The soluble carbohydrates are lichenin, and lichenin-starch or iso-lichenin. Lichenin gelatinises like starch, and by hydrolysis with acids is converted into dextrose with intermediate dextrins. Amylolytic enzymes have no action on it. From experiments on rabbits, the conclusion drawn is that it does not give rise to glycogen in the liver.

Isolichenin, which is obtained after filtering off the jelly formed by lichenin, is present in smaller quantity, gives a blue coloration with iodine, and somewhat resembles soluble starch. On hydrolysis with acid, it yields the same products as lichenin. With amylolytic enzymes, it forms dextrins, but no sugar.

W. D. H.

Palm Cake and Palm Cake Meal. By ADOLPH EMMERLING (*Landw. Versuchs-Stat.*, 1898, 50, 5—63).—*Acidity of palm cake.*—A number of samples of cake and meal were analysed and the results grouped according to the odour of the samples, some having a "fruity" odour, others being slightly rancid. The following average percentage results are given for (1) cake, (2) meal, and (3) crushed cake. The acid number represents milligrams of KOH per gram of fat.

	Proteids.	Fat.	Oleic acid.	Acidity.	Acid number.
Palm cake.....	17.12	7.85	2.36	32.0	63.4
Palm meal	16.49	8.19	3.83	48.5	96.6
Crushed cake	16.84	1.67	0.45	28.9	57.5

The acidity results, which are somewhat higher than those previously obtained (Nördlinger, *Abstr.*, 1890, 929; Heinrich, *2te. Ber. Landw. Versuchs-Stat. Rostock*, 1894; H. Fresenius, *Landw. Versuchs-Stat.*, 1891, 38, 296; and von Rümker, *Versuchs-Stat. Preussens*, i J., 1894) show

that, on the whole, the acidity of palm cake meal is higher than that of palm cake. The slightly rancid samples are somewhat more acid than the others, whilst the samples of a fruity odour are much more acid than those which did not have this odour. The acidity increases with decrease in amount of fat ; the amount of acid remains (on the average) constant.

In the case of earth-nut cake, Reitmair (Abstr., 1891, 770) found the cakes richest in acid contained a low percentage of fat. This does not hold good in the case of palm cake, probably owing to the processes of manufacture of the two products being totally different (compare Emmerling, *Landw. Versuchs-Stat.*, 1897, 49, 51).

With regard to the changes which take place when palm oil is kept, it was found that there was relatively little alteration in the amount of acid after two years. The volatile fatty acids increased slightly when the oil was exposed (4 months) to air. The iodine number diminishes when the oil is kept, and the change seems to be quickened under the influence of light. Exposure for 2 years considerably raised the acetyl number of palm oil. Palm cake kept for 2 years showed very little change in the amount of fat ; there was a very slight gain in proteids not to be accounted for by loss of water.

Acidity increased very greatly when the cake was kept, whether exposed to light or in darkness, and in closed vessels. The iodine number of the cake increased after prolonged exposure.

N. H. J. M.

Composition of Humus. By HARRY SNYDER (*J. Amer. Chem. Soc.*, 1897, 19, 738—744).—Humus prepared by mixing different kinds of organic matter with soil and keeping in a tight box for a year out of doors, was found to have the following composition.

Humus from :	C.	H.	N.	O.
Cow manure	41·95	6·26	6·16	45·65
Green clover	54·22	3·40	8·24	34·14
Meat scraps	48·77	4·30	10·96	35·97
Wheat flour	51·02	3·82	5·02	40·14
Oat straw	54·30	2·48	2·50	40·72
Sawdust	49·28	3·33	0·32	47·07
Sugar	57·84	3·04	0·08	39·04

The average composition of the ash of eight samples of precipitated humus was.

K ₂ O.	Na ₂ O.	CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	CO ₂ .	Insol.
7·50	8·13	0·09	0·36	3·48	3·12	12·37	0·98	1·64	61·97

A portion of the mineral matter is shown to have been derived from the soil.

Analysis of natural humus gave the following percentage results.

	C.	H.	N.	O.	Ash.
1. Rich prairie soil	45·12	3·67	10·37	28·60	12·24
2. Cultivated soil.....	48·16	5·40	9·12	33·16	4·16
3. Never cultivated.....	44·12	6·00	8·12	35·16	6·60
4. Cultivated (about 40 years)	50·10	4·80	6·54	33·66	4·90

N. H. J. M.

Physical Effects of Various Salts and Manure Constituents on a Soil as Modifying the Factors which Control its Supply of Moisture. By JASPER L. BEESON (*J. Amer. Chem. Soc.*, 1897, 19, 620—649).—The rates of saturation and of percolation were determined without, and after addition of small amounts of salts (various potassium, sodium, calcium, magnesium, and ammonium salts). The rate of evaporation, and the rate and extent of capillary "lift" were also determined under the different conditions.

In general, it was found that the four principal factors on which the moisture of soil depends (the rates of saturation, percolation, evaporation, and capillary rise) when altered by adding some salt, all vary in the same direction, whilst the capillary effect as shown by height varies in the opposite direction. The action of certain salts (sodium carbonate, for instance) in reducing the rate of percolation, &c., is due to the breaking up of the soil aggregates into smaller ones, and *vice versa*. At first sight, this seems opposed to the general experience that neutral salts precipitate fine clay when suspended in water, but in this case the soil particles have already been broken up, and only the finest are present.

Of the salts experimented with, those which most frequently occur in manures (potassium and ammonium sulphates and calcium superphosphate) would have very little effect on soil moisture when applied in the usual amounts, and their beneficial effect must be mainly due to the plant-food they contain. Sodium carbonate, chloride, and nitrate have, however, a much greater effect. These salts greatly decrease the rate of absorption of water, whilst they considerably increase the power of the soil in retaining moisture for the use of the crop; sodium nitrate is thus very suitable for soils which, at the same time, need nitrogen, and are not sufficiently retentive of moisture. More nitrogenous soil of a similar physical nature should be treated with sodium carbonate or chloride. Soil which is already too retentive would be injured by adding sodium nitrate to supply nitrogen. This explains why sodium nitrate often decreased the yield of sugarcane in Louisiana, whilst lime gave good results. N. H. J. M.

Proportions of Chlorine and of Nitrogen as Nitric Acid and as Ammonia in certain Tropical Rain-waters. By J. BURCHMERE HARRISON and JOHN WILLIAMS (*J. Amer. Chem. Soc.*, 1897, 19, 1—9).—Analyses of the rain in Barbados and British Guiana, made for several years in succession, gave the following average results (lbs. per acre).

	Average rainfall, inches.	N. as ammonia.	N. as nitrates.	Total nitrogen.	Chlorine.
Barbados	59·40	1·009	2·443	3·452	62·46
Brit. Guiana...	106·71	1·321	2·190	3·511	108·61

The highest and lowest results obtained were as follows (parts per million).

	N. as ammonia.		N. as nitrates.		Chlorine.	
Barbados	1·812	0·0	0·914	0·001	47·04	2·48
Brit. Guiana...	1·376	0·0	0·823	0·0	16·10	0·45

The total nitrogen (as nitrates and ammonia) per acre in the two colonies, situated in the tropics and in the direct course of the trade winds, is rather less than at Rothamsted (3.74 lbs. per acre); the relative amounts of nitrogen as ammonia and as nitrates is, however, very different. At Rothamsted, the nitrogen as nitrates amounts to rather over one-fourth of the total. In Barbados about three-fourths of the nitrogen is present as nitrates, and in British Guiana about two-thirds of the nitrogen is in this form. Comparing the results with those obtained at Tokio and in New Zealand, it is concluded that in tropical rain a higher proportion of the nitrogen is present as nitrates than in the case of the rain of temperate climates. In rain-water from Venezuela and Réunion, the nitrogen as nitric acid was found to be 0.578 and 0.69 per million respectively (Müntz and Marcano, *Abstr.*, 1889, 923).

It is concluded that, whilst the rain of the tropics is richer in nitric nitrogen than elsewhere, the total nitrogen supplied to the soil by the rain is not greater.

N. H. J. M.

Analytical Chemistry.

Apparatus for Gas Analysis. By THEODOR PFEIFFER and OTTO LEMMERMANN (*Landw. Versuchs.-Stat.*, 1898, 50, 143—158).—The apparatus employed for collecting and measuring the gases in the experiments on denitrification (this vol., ii, 445) is described, with sketches. It is constructed on the principle of weighing the amount of mercury corresponding with the volume of gas, instead of measuring the gas. The apparatus is suitable for dealing with large amounts of gas, and could be readily modified according to requirements.

N. H. J. M.

Volumetric Estimation of Combined Sulphuric Acid. By FERNAND TELLE (*J. Pharm.*, 1898, [vi], 7, 165—170).—In the method described by the author, the sulphuric acid is precipitated by adding a known volume of standard barium chloride solution, and the excess of the latter by an excess of a standard solution of potassium dichromate, rendered alkaline by the addition of ammonia free from carbonate; the unprecipitated potassium chromate is then estimated by determining, by means of sodium thiosulphate, the amount of iodine it is capable of liberating from potassium iodide. The standard solutions used should be of equivalent concentrations; if the barium chloride is decinormal, the solution of potassium dichromate should contain 7.358 grams of the pure salt per litre, whilst the thiosulphate solution, standardised by means of the latter, should contain about 38 grams of the crystallised salt ($+5\text{H}_2\text{O}$) per litre.

To determine the sulphuric acid in a natural water, 500 c.c. of the latter is evaporated, after the addition of 4—5 c.c. of hydrochloric acid, until the volume is about 10 c.c., and is then decanted into a

110 c.c. flask, the residue being carefully washed with the least possible amount of water; 10 c.c., or a sufficient excess, of the barium chloride is added, the liquid boiled and rendered alkaline by ammonia, and 100 c.c. of the dichromate solution added. The solution is again boiled, then cooled and made up to 110 c.c., and filtered; to 100 c.c. of the filtrate, acidified with hydrochloric acid, 5 c.c. of 10 per cent. potassium iodide solution is added, and the liberated iodine estimated by the solution of thiosulphate, the end-reaction with starch solution being quite sharp. Allowance has, of course, to be made for the fact that 100 c.c. only of the original 110 c.c. containing free chromate was used for the titration. In the case of waters containing a large amount of organic matter, the latter has to be oxidised by potassium chlorate during the preliminary evaporation, when the volume is about 50 c.c., care being taken to expel completely the chlorine produced during this oxidation.

The potassium sulphate present in a wine-extract can be determined by a similar method; the results obtained are, however, slightly high, owing to the presence of traces of phosphoric acid in the extract.

W. A. D.

Simultaneous Volumetric Estimation of Sulphuric Acid and Calcium Salts in Water. By LUCIEN ROBIN (*J. Pharm.*, 1898, [vi], 7, 283—286).—To 100 c.c. of the water contained in a measuring flask with the neck widened above the graduation mark, 0.5—1.0 c.c. of a solution containing 100 grams of sodium carbonate and 50 grams of pure caustic soda dissolved in 300 c.c. of water is added, the mixture boiled during five minutes, and, after cooling, diluted to 100 c.c.; the precipitate is removed by filtration, and 50 c.c. of the filtrate taken for the determination of the sulphuric acid. This is carried out by neutralising with hydrochloric acid, boiling to expel carbonic anhydride, neutralising again with ammonia, and precipitating with an excess (10 c.c.) of half-decinormal barium chloride; after standing for 15 minutes, the solution is again boiled, and 10 c.c. added of a solution prepared by saturating with ammonia 3.69 grams of potassium dichromate dissolved in a litre of water. The liquid is then filtered, 20 c.c. of a solution containing 10 grams of ferrous sulphate per litre added, and the amount of the latter remaining unoxidised determined by standard potassium permanganate.

To estimate the calcium salts, the precipitate obtained from the original 100 c.c. of water is dissolved in hydrochloric acid, the solution rendered alkaline by ammonia, and 10 c.c. of decinormal ammonium oxalate added; after standing 30 minutes, the excess of ammonium oxalate can be determined in the filtrate by acidifying with nitric acid, and titrating against permanganate; or the calcium oxalate can be dissolved in dilute nitric acid, and the oxalic acid liberated determined by the same method.

W. A. D.

Detection and Estimation of Sulphurous and Thiosulphuric Acids. By WILHELM AUTENRIETH and A. WINDAUS (*Zeit. anal. Chem.*, 1898, 37, 290—300).—For qualitative separation, use may be made of the wide difference in the solubility of the strontium salts of the

above two acids. The sulphite requires 30,000 parts, the thiosulphate 3·7 parts of water for solution. A mixture of the alkali salts of the two acids is therefore treated with excess of strontium nitrate or chloride, shaken vigorously, filtered after a few minutes through a double filter, and the precipitate well washed. The thiosulphate in the filtrate is recognised by the precipitation of sulphur on decomposing with hydrochloric acid, the sulphite in the precipitate by dissolving in dilute acid and oxidising with iodine to sulphate, either with or without previous addition of barium chloride.

For quantitative estimation, a solution containing the two salts is titrated with iodine: a second portion of the same solution is mixed with excess of strontium nitrate, made up to a known volume, shaken, filtered after some hours through dry paper and an aliquot part of the filtrate titrated as before. By deducting 0·4 c.c. of N/10 iodine per 100 c.c. from the last titration to correct for the solubility of strontium sulphite, very fair results are obtained. M. J. S.

Detection of Nitric Acid in Human Remains. By ANTON SEYDA and R. WOY (*Chem. Centr.*, 1897, ii, 1036—1037; from *Zeit. öffentl. Chem.*, 3, 487—493).—If possible, the urine should be tested for nitrous acid by distilling it with dilute sulphuric acid, collecting the distillate in a flask containing aqueous soda, using Griess' well-known test. Another portion is then boiled with hydrochloric acid and ferrous chloride, and the gases passed into a separating funnel filled with mercury, and also containing a little aqueous soda. The mercury is afterwards displaced by means of a current of oxygen, and the alkaline solution again tested for nitrous acid; if the reaction is now very much stronger, it may be safely assumed that nitric acid was present.

Other portions of the body, finely comminuted, are twice macerated with water, and the liquid, filtered through cotton wool, is mixed with a slight excess of lime and evaporated to a syrupy consistence; this syrup is then extracted with alcohol to dissolve the calcium nitrate, and after evaporating the spirit, the residue is dissolved in a known volume of water and the solution used for the detection or estimation of the nitric acid. The method best suited for the estimation of the nitric acid is the well-known Schlösing-Schulze process. Methods based upon its conversion into ammonia cannot be employed, as it is impossible to free the liquid from ammonia by distillation with potash. L. DE K.

Detection of Phosphorus. By H. NATTERMANN and ALBERT HILGER (*Chem. Centr.*, 1897, ii, 981—982; from *Forsch. Ber. Lebensm. Hyg.*, 4, 241—258).—The authors have slightly modified Mitscherlich's apparatus. By means of a 30 cm. glass tube, furnished with india-rubber connections and a screw clamp, air is drawn through the apparatus until phosphorescence sets in, when a current of carbonic anhydride is substituted for the air, and the liquid in the flask is heated to boiling. Besides causing the phosphorescence to be more plainly visible, the process has the further advantage that more than 90 per cent. of the phosphorus may be recovered from the distillate.

They have also modified Dussard-Blondlot's method. A 100 c.c. wide-necked flask containing the supposed silver phosphide precipitate, and also some zinc and water, is closed by means of a cork perforated with three holes; through two of these pass rectangularly bent tubes which do not penetrate below the cork. A current of hydrogen generated from a Kipp's apparatus is passed in through one of them and out by the other, which is connected with a U-tube containing pumice-stone drenched with aqueous potash, this in turn being connected with a glass tube furnished with a platinum jet. The third opening is fitted with a safety funnel. After the hydrogen flame has been carefully tested and found to be free from any green colour, dilute sulphuric acid (1:5) is admitted through the safety-funnel, and this, if phosphorus be present, will cause the liberation of hydrogen phosphide from the silver phosphide, and the flame will become greenish.

L. DE K.

Rapid Estimation of Phosphorus. By HENRYK WDOWISZEWSKI (*Chem. Centr.*, 1897, ii, 1038; from *Stahl. u. Eisen*, 1897, 814—815).—Two grams of pig iron dissolved in 30 c.c. of nitric acid of sp. gr. = 1.2 is diluted to 50 c.c. with water, filtered from the undissolved silicic acid and graphite, and boiled down to the original bulk; it is then oxidised with potassium permanganate, mixed with hydrochloric acid, and, when cold, neutralised with ammonia. After heating to 60°, molybdate solution is added, the whole shaken for 5 minutes and the yellow precipitate collected and washed with a 10 per cent solution of ammonium nitrate. It is then dissolved in ammonia, and after partly neutralising with hydrochloric acid, a few c.c. of magnesia mixture and an excess of ammonia are added. The closed flask is then allowed to stand for 15 minutes in ice, shaken for 5 minutes, and the precipitate at once collected on a filter. After being washed with dilute ammonia, it is dried, ignited, and weighed.

L. DE K.

Estimation of Phosphoric Acid as Phosphomolybdic Anhydride. By P. NEUMANN (*Zeit. anal. Chem.*, 1898, 37, 303—308).—From the experiments of Woy (this vol., ii, 138), it appears that the large excess of ammonium molybdate commonly employed is not necessary; 20 per cent. above the theoretical amount for the production of $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$, or about 36 parts for one part of P_2O_5 , being sufficient. In the analysis of ferruginous phosphates (basic slag), Woy's method gives somewhat lower results than the ordinary process, in which the phosphoric acid is finally precipitated as ammonium magnesium phosphate. This deficiency seems to be attributable to the presence (in the yellow precipitate) of iron phosphate, the molecular weight of which is much lower than that of the molybdenum compound. By employing the following process, results have been obtained agreeing very closely with those in which the precipitate was weighed as magnesium pyrophosphate.

Fifty c.c. of the cold phosphate solution (containing about 0.5 gram of substance) is nearly neutralised with ammonia, then mixed with 120 c.c. of the ordinary molybdate solution, and stirred in the cold for 15 minutes. The precipitate is then washed three times by decantation

with a solution containing 5 per cent. of ammonium nitrate and 1 per cent. of nitric acid, and rinsed into a Gooch crucible with the same liquid. The Gooch crucible, placed inside an ordinary porcelain crucible, is exposed to a gradually rising temperature for about 25 minutes, during the last 15 of which the flame of the Bunsen burner completely surrounds it. The bluish-black residue has the formula $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$.
M. J. S.

Ignition of Ammonium Magnesium Phosphate. By MAX SCHMOEGER (*Zeit. anal. Chem.*, 1898, 37, 308—310).—In igniting the precipitate obtained in a phosphoric acid estimation, it is customary to detach it from the filter as completely as possible, burn the latter in a coil of platinum wire, and raise the temperature of the crucible containing the precipitate very gradually. These precautions are quite unnecessary. After shaking out most of the precipitate into the crucible, the paper filter may be folded together and added to the precipitate. The cover is then placed on the crucible and the latter at once exposed to the full flame of a Bunsen burner; a little later, it is placed obliquely, and is finally heated with the blow-pipe flame. A white pyrophosphate is quickly and easily obtained; the weight agrees accurately with that resulting from the most cautious ignition, and no action on the platinum crucible is perceptible.
M. J. S.

Colorimetric Estimation of Silica in Water. By ADOLF JOLLES and FRIEDRICH NEURATH (*Zeit. angew. Chem.*, 1898, 315—316).—The process is based upon the yellow coloration noticed when solutions of silicic acid are heated with a nitric acid solution of molybdic acid. Eight grams of potassium molybdate is dissolved in 50 c.c. of water and poured into 50 c.c. of nitric acid of sp. gr. = 1.2. Twenty c.c. of the sample of water is put into a test-tube of such size that the column of liquid will be about 18 cm. high; 1 c.c. of the molybdate solution is then added. Similar tubes are taken containing distilled water, with varying small quantities of silicic acid in the form of an alkali silicate, and to each, 1 c.c. of the reagent is added. On warming to 80°, the colour will make its appearance, and the tubes are then compared as usual. The amount of phosphoric acid in waters that have not been concentrated is so small that it does not interfere with the reaction.
L. DE K.

Alkalimetric Estimation of Metals. By HENRI LESCŒUR (*Bull. Soc. Chim.*, 1897, [iii], 17, 26—55).—The volumetric estimation of metals forming oxides soluble in water presents no special difficulty, and the nature of the indicator employed is immaterial. In the case of metals forming insoluble oxides, however, litmus cannot be used, owing to the formation of unstable compounds of the oxide with the indicator, and there is an important distinction between the results obtained by the use of helianthin, on the one hand, and phenolphthalein on the other. When alkali is gradually added to a liquid containing an insoluble oxide and excess of acid in presence of phenolphthalein, the red coloration of the latter does not make its appearance until the free acid has been neutralised and the whole of the oxide precipitated. Phenolphthalein, therefore, is an indicator of the transition from neu-

trality to alkalinity. Helianthin, on the other hand, indicates the passage from acidity to neutrality, the end point being reached when the free acid has been neutralised, and the precipitation of the oxide is about to commence. If both indicators are present in the solution, the amount of alkali added between the two end points is proportional to the metallic oxide present. An insoluble base may be titrated directly by means of standard acid and helianthin, but as solution takes place slowly, it is generally advantageous to dissolve in a known excess of acid and titrate back with alkali. A similar procedure is sometimes required when phenolphthalein is employed, especially when there is a tendency to the formation of basic salts, or when the insoluble oxide is coloured; in this case, the solution is boiled with excess of alkali, filtered, and the filtrate titrated back with standard acid.

The accuracy of the results obtained by the use of phenolphthalein is liable to be adversely affected by the presence of carbonic anhydride, and the carrying down of undecomposed salt by the precipitated oxide. These sources of error are to be avoided by working with sufficiently dilute solutions, free from carbonic anhydride, and by operating at the boiling temperature. It is also to be noted that some oxides, such as those of magnesium, silver, and lead, usually regarded as insoluble in water, are sufficiently soluble to affect phenolphthalein. The indications of helianthin are not so sharp as those of phenolphthalein, and are very obscure in the presence of feeble acids and of ferric oxide; for this reason, oxalic acid is not so well adapted for alkalinity as the mineral acids. The standard alkali should be free from carbonate and alumina or other oxides. The use of baryta offers certain advantages, its strength undergoes alteration from absorption of carbonic anhydride, but remains independent of the nature of the indicator. Barytes is not sufficiently soluble to allow of a normal solution being obtained, but a mixture of baryta and soda answers equally well. The use of picric acid is recommended for standardising the solutions, as it is easily obtained pure and has a high molecular weight, 229. The chief disadvantage attending its use is its sparing solubility, 400 c.c. of water being required for the solution of 2.29 grams. In the comparison of the standard acid and alkali with each other, the intervals between the end points indicated by phenolphthalein and helianthin should not correspond with more than one or two drops of N/10 solution. The absence of appreciable amounts of carbonic anhydride or alumina is thus proved.

Estimation of Magnesium.—As magnesium oxide is sufficiently soluble to affect phenolphthalein, magnesia, obtained by precipitation with sodium hydroxide and subsequent washing with water, may be titrated directly by using phenolphthalein and adding standard acid until the red colour is discharged; but as the oxide dissolves slowly, it is better to boil the precipitated magnesia, or magnesium carbonate, with excess of standard acid and titrate back with alkali. If other metals are present along with magnesium, phenolphthalein is added to the solution, and then alkali until the red colour appears. The precipitated oxides are filtered off, and the magnesia, which is left in solution, is precipitated by further addition of alkali, and estimated as before.

Magnesia is best separated from alumina by boiling with excess of caustic soda, whilst lime must be removed by means of ammonium carbonate, since it is partially precipitated along with magnesia by caustic soda.

Estimation of Zinc.—[With CL. LEMAIRE.]—The results obtained by previous observers are criticised, and the following methods are stated to give the most satisfactory results. (1) The solution is boiled with excess of sodium carbonate, filtered, and the washed precipitate, together with the filter, treated with excess of standard acid and titrated back with alkali, using helianthin as the indicator. (2) Both indicators are added, and then standard alkali until the red tint of the helianthin disappears. Excess of alkali is now added, the solution boiled, and titrated back with acid until the end point indicated by phenolphthalein is reached. The alkali used between the two end points corresponds with the zinc present. Instead of weighing the oxide or sulphide of zinc obtained in the usual gravimetric processes, it is recommended that the moist precipitates be dissolved in hydrochloric acid, boiled, and treated by method 2; the error arising from the presence of alkali in an imperfectly washed precipitate is thus avoided.

Estimation of Lead.—[With DELSAUX.]—The direct titration of lead salts with caustic alkalis is unsatisfactory, owing to combination taking place between the phenolphthalein and oxide of lead. Good results, however, are obtained by using sodium carbonate at the boiling temperature. Helianthin may also be used, the lead being precipitated as oxide or carbonate, washed, dissolved in excess of acid, and titrated back with alkali. If free acid be present, sodium carbonate is run in until the red tint of helianthin is discharged; the solution is boiled, and the titration continued to the end point indicated by phenolphthalein. Lead sulphate may be titrated in precisely the same manner, although the reaction takes place somewhat slowly, and this process is useful in connection with the separation of lead from other metals. In the presence of the alkaline earths, the sulphates of which are also insoluble, the lead is to be precipitated by caustic alkali added in very slight excess, and the washed precipitate treated as above described.
N. L.

Estimation of Potash in Potash-manures. By LÉON RONNET (*Chem. Centr.*, 1897, ii, 1157—1158; from *Rev. Chim. anal. applic.*, 5, 421—422).—*Assay of Potassium Chloride.*—Fifty grams of the sample is dissolved, made up to 1 litre, and filtered; 20 c.c. of the filtrate is mixed with 10 c.c. of saturated baryta water and the excess of barium is then removed by a current of carbonic anhydride. After boiling for a few minutes, the liquid is filtered and the potash is then estimated in the usual way with perchloric acid.

Assay of Potassium Sulphate and Kainite.—Instead of 10 c.c. of baryta water, 40 c.c. is used, and the operation is conducted as before.

Assay of mixed Manures.—Twenty-five grams of the manure is dissolved, made up to 500 c.c. and filtered. 100—200 c.c. of the liquid is dried in a porcelain dish with 1—2 grams of calcium hydroxide, incinerated at the lowest possible temperature, the residue dissolved in boiling

water, and the filtrate, which is kept boiling, is then treated with baryta as described.

L. DE K.

Detection of Sodium Carbonate in Sodium Phosphate. By GEISSLER (*Zeit. anal. Chem.*, 1898, **37**, 323; from *Pharm. Centralh.*, **34**, 729).—Phenolphthalein will detect 1/10 per cent. of sodium carbonate in disodium hydrogen phosphate, which latter, when pure, gives no pink colour with the indicator. The test with ammonium chloride and magnesium sulphate, sometimes recommended, is fallacious.

M. J. S.

Analysis of Sodium Sulphide. By FERDINAND JEAN (*J. Pharm.*, 1898, [vi], **7**, 170—172).—Ten grams of the coarsely powdered sample is dissolved in water, and, after removing the insoluble substances by filtration, diluted to a litre. The quantity of iodine corresponding with the sodium sulphide, polysulphides, and thiosulphate in 10 c.c. of the solution is then determined by direct titration. The sodium monosulphide present in the 10 c.c. is estimated by adding as many c.c. of a solution containing 6·7 grams of ammonium sulphate per litre as were employed in the iodine titration, diluting with 30 c.c. of water, and distilling the ammonia liberated into 20 c.c. of decinormal acid; the distillate is then boiled to expel hydrogen sulphide, and the excess of acid determined. Each cubic centimetre of acid neutralised by the ammonia corresponds with 0·0039 gram Na_2S . The residue in the distilling flask is then titrated against decinormal iodine, and the quantity of sodium thiosulphate in the original 10 c.c. determined. The difference between the first and second iodine titrations is a measure of both the monosulphide and polysulphides present, and is best expressed in terms of the former. The value so obtained is always greater, unless no polysulphides are present, than that obtained for the monosulphide by the ammonia distillation, since the latter only determines monosulphide present as such. The difference between the two values indicates an excess of monosulphide corresponding with the polysulphides, so that it is best expressed as sulphur. Since both the monosulphide and polysulphides of sodium behave in the same way towards ammoniacal zinc solution, the same results are obtained by titration against the latter as were obtained with iodine.

W. A. D.

Microchemical Detection of Magnesia. By GYSBERT ROMIJN (*Zeit. anal. Chem.*, 1898, **37**, 300—301).—Traces of magnesium may be detected in presence of cobalt, iron, chromium, aluminium, and the alkali metals, by adding a little citric acid, and excess of ammonia, evaporating to dryness without regard to any precipitate which may form, dissolving the residue in ammonia (diluted with 10 volumes of water), and adding a fragment of sodium phosphate. The crystals obtained at any dilution exhibit under the microscope the hemimorphic forms described by Behrens, together with a highly characteristic twin combination, of which a figure is given. The presence of much zinc is an obstacle to the microchemical detection of magnesia.

M. J. S.

Electrolytic Estimation of Cadmium. By EBERHARD RIMBACH (*Zeit. anal. Chem.*, 1898, 37, 284—290).—The author reports his experience of the cyanide method of Beilstein and Jawein (*Abstr.*, 1879, 746) which he pronounces to be a perfectly satisfactory one. The cadmium may be in the form of either chloride or sulphate; the neutral solution is to be treated with an excess (about 3 grams) of 98 per cent. potassium cyanide and electrolysed at ordinary temperatures with a current of 0.02—0.04 ampère and a potential of 3—3.3 volts, which may either be supplied from a storage battery or from 3—5 Meidinger elements. In 12—16 hours, quantities of metal up to 0.4 gram can be deposited, and in all cases the metal is deposited in a coherent and lustrous layer, no trace of spongy metal ever being obtained. That the current is strong enough may be judged from the solution acquiring a dark brown colour; but too strong a current leads to the deposition of black stains, whilst the platinum cathode is slightly attacked. Should copper be present, that metal is not precipitated until all the cyanide is decomposed. In this case, 5 grams of cyanide should be added, and a very satisfactory estimation of both metals can be made. Should the metals be present as nitrates, conversion into chlorides is desirable. In presence of magnesium, addition of ammonium chloride prevents the deposition of any of that metal. M. J. S.

Estimation of Traces of Lead in Sugar and Saccharine Liquors. By ALEXANDER KOLLREPP (*Chem. Centr.*, 1897, ii, 1160; from *N. Zeit. Rüb. Zuck. Ind.*, 38, 126—128).—If hydrogen sulphide is passed through a saccharine liquid containing a trace of lead, the lead sulphide is so finely divided that it cannot be filtered off, but it may be precipitated by adding to the liquid a mixture of paper pulp and aluminium hydroxide. The author now proposes using white of egg; 500—1000 grams of sugar is dissolved in water to 30—40° Brix, and after passing hydrogen sulphide for half an hour and allowing the liquid to remain for another 3 hours, solution of white of egg is added, and the whole boiled; if the liquid is alkaline, it must be previously neutralised with acetic acid. The precipitate is collected, washed with a weak solution of hydrogen sulphide, dried, and incinerated; the ash is then moistened with water, a little sodium carbonate added, and the whole gently ignited; by treating the residue repeatedly with water, any sulphuric acid is removed, and the undissolved portion together with the filter is again ignited, and then digested for half an hour with boiling concentrated nitric acid. After diluting and filtering, the liquid is evaporated nearly to dryness, the residue extracted with water, and the lead tested for with hydrogen sulphide.

The amount of lead found by the author in juices which had been treated by Wohl's lead oxide process was quite insignificant.

L DE K.

Detection and Estimation of Traces of Lead in Beet Sugar. By GEORG KASSNER (*Chem. Centr.*, 1897, ii, 1160—1161; from *Dingl. Pol. J.*, 298, 303).—The author states that traces of lead in beet sugar may be detected and estimated by Kollrepp's process (see preceding abstract).

L. DE K.

Volumetric Estimation of Chromium. By RUDOLF L. LEFFLER (*Chem. News*, 1898, **77**, 156—157).—Galbraith's method of estimating chromium in steel or iron by dissolving the metal in dilute sulphuric acid, oxidising the ferrous sulphate formed with potassium permanganate and the chromic oxide by the further use of an equal quantity of the same reagent, filtering, adding ferrous salt to the filtrate, and titrating back with potassium dichromate, is shown to give results varying with the proportion of acid used for solution, and also with the magnitude of the excess of permanganate employed. It is necessary to make a blank experiment under exactly the same conditions as those used in the analysis, and to subtract the value so obtained from the amount of chromium found. D. A. L.

Separations from Chromic Acid. III. Separation of Aluminium. By HARRY BREARLEY (*Chem. News*, 1898, **77**, 179—180. Compare this vol., ii, 409).—With potassium chromate and aluminium chloride in hot solutions, the author finds, as other workers have done, that no permanent precipitate forms until five equivalents of chromate have been added; with cold solutions, however, even a small amount of chromate gives a precipitate which only dissolves tardily and never completely; with iron, the reverse is the case (compare *loc. cit.*). Aluminium hydroxide reacts with potassium chromate, therefore the separation of chromium and aluminium is imperfect unless alkali is used in excess. The recovery of chromium from solutions containing 0.5 gram of aluminium and 50 c.c. of potassium chromate (1 c.c. = 0.05 Fe) amounted to 99 per cent. with an excess of 30 c.c. of 2N sodium carbonate, but was less with smaller excess of this alkali, or when ammonia or ammonium carbonate was used. For aluminium estimations, however, it is pointed out that the quantity of aluminium hydroxide dissolved is greater the greater the excess of alkali, and that sodium carbonate is more active in this direction than the other alkalis. The separation of chromium from aluminium by means of sodium acetate is imperfect, since, when neutralised not only is there an error due to the reaction of the chromate with aluminium chloride, but also that due to the reaction between the latter and the aluminium hydroxide, whereas, when not neutralised, much aluminium is dissolved. With sodium phosphate, however, following Carnot's instructions, or even in neutralised solutions, the separation is satisfactory; but 20 c.c. of saturated sodium phosphate is not sufficient to precipitate 0.5 gram of aluminium; therefore to separate chromium and aluminium, the use of ammonia or ammonium carbonate or of any method involving the precipitation of aluminium from a neutral solution should be justified or abandoned. From what has been shown, it is evident that the separation of alumina and ferric oxide together from chromic anhydride cannot be effected by sodium carbonate, sodium hydroxide, or sodium phosphate without modifications of the present methods; the sodium phosphate separation becomes effective by treating the solution so as to just neutralise the free acid without the formation of any dissolved ferric hydroxide, a state indicated by the change of colour; under these conditions, and with 0, 2, and 5 per

cent. of acetic acid, nearly perfect chromium recoveries were obtained from mixtures of equivalent proportions of ferric chloride and potassium chromate.
D. A. L.

Volumetric Estimation of Metallic Sulphides. By Jos. HANUS (*Zeit. anorg. Chem.*, 1898, 17, 111—116).—The method consists in treating the precipitated sulphide with ferric sulphate or chloride, and titrating the ferrous solution so obtained with permanganate.

In the estimation of antimony, the reaction takes place according to the equation $\text{Sb}_2\text{S}_3 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} = 2\text{H}_3\text{SbO}_4 + 10\text{FeSO}_4 + 5\text{H}_2\text{SO}_4 + \text{S}_3$. From 0.2—0.9 gram of antimony sulphide is boiled for 15 minutes with an excess of ferric sulphate, and, after cooling, sufficient sulphuric acid added to dissolve the precipitate and the solution made up to 200 c.c.; 100 c.c. is then filtered through a dry filter, and titrated with permanganate. The results are accurate. The antimony, in mixtures of antimony sulphide and sulphur, can be estimated by this method, as the sulphur has no influence on the result. It is important that the antimony sulphide precipitate should not be exposed to the air, as ferric sulphate is without action on the oxysulphide.

Ferric sulphate also reacts with the sulphides of lead, mercury, copper, cadmium, tin, arsenic, and bismuth. The author has obtained accurate results by this method with lead and bismuth sulphides. Mercury and arsenic sulphides are only partially oxidised, even after prolonged action. With copper sulphide, the author could not obtain accurate results with ferric sulphate, and with ferric chloride 99 per cent. of the copper was determined, but the blue colour of the solution greatly interferes with the titration.
E. C. R.

New Method of Estimating Bismuth. By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1898, 31, 1303).—Formalin (formaldehyde solution) and a large excess of soda are added to the slightly acid bismuth solution, and the whole is heated on the water bath and stirred until the liquid has become clear, after which a little more formalin and alkali is added, and the heating is continued for a few minutes over a bare flame. The spongy precipitate of metallic bismuth is washed repeatedly by decantation, pressed together with a glass rod, collected on a tared filter, washed with absolute alcohol, dried at 105°, and weighed. The method is simpler than the usual ones, and quite as accurate; in the analyses quoted, the maximum error is ± 0.1 per cent. of the weight of the bismuth.
C. F. B.

Estimation of Methane in Fire-damp. By EDUARD HANKUS (*Chem. Centr.*, 1897, ii, 987; from *Österr. Zeit. Berg. Hütt.*, 45, 548—549).—The sample should be collected in a glass, and not in a tin, vessel, as when the latter is used it is not possible to see whether any deposit is formed on the sides of the vessel. If there is such a deposit, it may cause the complete absorption of the methane, but if there is none, the gas may be kept for some 18 days without undergoing any diminution in volume. Excess of methane will always be noticed after a sudden fall of the barometer.
L. DE K.

Estimation of Ferrocyanogen. By LEONARD DE KONINGH (*Zeit. angew. Chem.*, 1898, 463—464).—The process is based on the fact that the insoluble ferrocyanides are decomposed by heating with aqueous potash, yielding potassium ferrocyanide. The latter, when fused with saltpetre, yields ferric oxide, which may be estimated with great accuracy, and the amount of ferrocyanogen calculated from it. If the sample contains Prussian blue, it is likely to contain also lead chromate; this also dissolves in the potash, but the lead may be removed by means of sodium sulphide, the chromium passing all but completely into the melt. The undissolved ferric oxide must not be weighed without further purification, which is best effected by dissolving it in hydrochloric acid, adding citric acid, and finally ammonia and ammonium sulphide. The iron sulphide is then converted into oxide by ignition.

The author points out the difficulty experienced when testing commercial Prussian blue. If it contains much alumina, it is impossible to state with certainty whether part of the "ferrocyanogen" found is not really the valueless aluminium compound. Then, again, even the most carefully prepared blue is a mixture of the real ferric ferrocyanide with ferric hydroxide and alkali ferrocyanide. An experiment is described from which it would appear that 1 part of ferric oxide corresponds with about 5 parts of commercial Prussian blue. L. DE K.

Volumetric Estimation of Glycerophosphates. By A. ASTRUC (*J. Pharm.*, 1898, [vi], 7, 5—8).—Although solutions of calcium glycerophosphate are always alkaline to methyl-orange, they are sometimes acid and sometimes alkaline towards phenolphthalein; in the latter case, the alkalinity is very feeble, whereas, when acid, a considerable quantity of caustic soda is required for neutralisation. When either the acid or alkaline salts have been exactly neutralised in presence of phenolphthalein, the amount of sulphuric acid subsequently required to produce a neutral tint with methyl-orange corresponds with the equation $2\text{Ca}(\text{C}_3\text{H}_7\text{O}_2\text{PO}_4) + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{CaH}_2(\text{C}_3\text{H}_7\text{O}_2\text{PO}_4)_2$. When the solution of the glycerophosphate has, in the first place, been rendered neutral to methyl-orange by a mineral acid, the amount of caustic soda required to produce a pink coloration with phenolphthalein corresponds with the equation $\text{CaH}_2(\text{C}_3\text{H}_7\text{O}_2\text{PO}_4)_2 + 2\text{NaOH} = \text{CaNa}_2(\text{C}_3\text{H}_7\text{O}_2\text{PO}_4)_2 + 2\text{H}_2\text{O}$, or $= \text{Ca}(\text{C}_3\text{H}_7\text{O}_2\text{PO}_4) + \text{Na}_2(\text{C}_3\text{H}_7\text{O}_2\text{PO}_4) + 2\text{H}_2\text{O}$.

In either of the above cases, 2 molecules of sodium hydroxide correspond with 1 molecule of phosphoric anhydride. By using the second reaction, the author finds that the amount of the latter present in samples of calcium glycerophosphate can be determined with a fair degree of accuracy, providing, of course, that the salt is not adulterated with other metallic phosphates or phosphoric acid. W. A. D.

Volumetric Estimation of Glycerophosphates. By ADRIAN and AUGUSTE TRILLAT (*J. Pharm.*, 1898, [iv], 7, 163—165, and 225—226. Compare preceding abstract, and this vol., i, 222).—The authors describe a method for estimating glycerophosphates of the

alkaline-earths, which is substantially identical with that depending on the first equation in the preceding abstract.

The presence of glycerol does not interfere with the use of methyl-orange or phenolphthalein as indicators for estimating phosphoric acid by titration against alkalis. When phosphoric acid is mixed with normal or acid glycerophosphates, the amount of alkali required for neutralisation corresponds, when either methyl-orange or phenolphthalein is used as an indicator, with the sum of the quantities required by the constituents of the mixture. W. A. D.

Estimation of Glucose in Urine by Means of Methylene-blue. By GOFF (*Chem. Centr.*, 1897, ii, 1062; from *Rép. de. Pharm.*, 1897, 250).—Although urine decolorises methylene-blue, it has no such action if it has been previously strongly diluted. Urine may, therefore, be tested for glucose by adding to 1 c.c. of the diluted sample (1:3) 5 c.c. of a solution of methylene-blue (1:5000) containing a few drops of aqueous potash. Normal urine remains blue, but diabetic urine is at once decolorised or turns pale yellow. To render this reaction quantitative, 30 c.c. of methylene-blue solution mixed with 1 c.c. of 4·5 per cent. aqueous potash is added drop by drop to 1 c.c. of diluted urine, covered with a little xylene, and placed in boiling water until there is a permanent blue coloration. The xylene serves to protect the solution from atmospheric oxygen. The sample of urine should not contain more than 0·3 per cent. of glucose. One c.c. of a 0·1 per cent. solution of glucose requires 6·5 c.c. of the reagent. Urea, uric acid, sodium chloride, creatinine, peptones, albumin, do not reduce the blue; biliary matters turn it green. L. DE K.

[Analysis of Sugar-cane Juice.] By C. H. PELLET (*Bied. Centr.*, 1898, 27, 357).—See this vol., ii, 447.

Detection and Estimation of Starch in Opium. By LYMAN F. KEBLER and CH. H. LAWALL (*Chem. Centr.*, 1897, ii, 985; from *Amer. J. Pharm.*, 1897, 234).—Ten grams of opium is extracted with cold water, and then heated on the water bath with some alcoholic potash; the liquid is filtered hot, and after being freed from alcohol by evaporation, is acidified with hydrochloric acid, the whole boiled in a reflux apparatus for 3 hours. It is then neutralised with aqueous soda, made up to a definite bulk, and an aliquot part treated with Fehling's solution, either gravimetrically or volumetrically. It should be noted, however, that pentoses and other carbohydrates also yield glucose. L. DE K.

Estimation of Dry Matter in Beer and Worts, and the Relation of Dry Matter to Specific Gravity. By C. N. RIIBER (*Bied. Centr.*, 1898, 27, 336—339; from *Christiania Videnskabs selskabs Skr. I. Math.-Naturw. Klasse*, 1897, No. 5, 1—82).—The substance is dried under diminished pressure in a current of dry air. When heated for 1½ hours at 100° under 20 mm. pressure the error is at most 0·02 per cent. Very exact results are obtained by heating for 2 days at 80°; the error does not then exceed 0·005 per cent.

When there is a certain quotient between the amounts of dry

matter of two solutions of the same sp. gr., the same quotients are found whatever the sp. gr. is; so that it is possible to construct a table for any beer extract, &c., by means of a single fundamental formula. A formula can then be obtained representing the relation between the sp. gr. and the amount of extract in the solution. As this relation varies according to the chemical composition and the mode of preparation of the worts and extracts, special formulæ must be calculated for exact determinations of extract by means of the sp. gr. The differences in the various groups (worts, (1) boiled, (2) not boiled, (3) partly fermented, and (4) completely fermented) are, however, so slight that, for practical purposes, a single table may be used. A table was made showing every sp. gr. between 1.0000 and 1.0859 for boiled worts, and the amount of extract shown by it never differed from the actual amount by more than 0.01 per cent. The formula in this case is $S = 1 + 0.0039921e + 0.000015136e^2$, in which S is the sp. gr. and e the amount of extract per cent. N. H. J. M.

Estimation of Aldehydes in Spirit by Means of Phenols. By E. BARBET (*Chem. Centr.*, 1897, ii, 1163; from *Bull. Assoc. des Chim. Sucre et Distill.*, 14, 943).—A few c.c. of a phenol, or a phenolic compound, is put into a test-tube and 2 c.c. of the spirit to be examined is added. After the phenol has dissolved, 1 c.c. of pure sulphuric acid is carefully run down the side of the tube and allowed to collect at the bottom; if aldehydes are present, coloration will be produced where the two layers meet. The tube is then shaken to mix the liquids, and a coloration is noticed depending on the nature of the reagent and the aldehyde, and, as regards its intensity, on the quantity of the latter. The colour produced by phenol and acetaldehyde is a beautiful heliotrope; if resorcinol or thymol is used, a pale blue ring is obtained, with pyrogallol a violet wine-red, and with phloroglucinol an intense red is noticed. Formaldehyde is detected by means of gallic acid. Certain phenols give almost the same colours with the different aldehydes, for example, naphthol, quinol, and phloroglucinol; these reagents may therefore be used for the colorimetric estimation of the joint aldehydes. The author has, as yet, only checked the method with pure acetaldehyde and acetaldehyde.

The detection of the nature of the aldehyde is important, as it gives a clue to the probable origin of a sample of spirit. L. DE K.

Estimation of the Acidity of Beer or other Liquids containing Acid Phosphates. By ADOLF OTT (*Chem. Centr.*, 1897, ii, 1121 and 1200; from *Zeit. ges. Brauw.*, 20, 540—543, 549—552, 572—573).—The author states that the acidity of some German beers is to a large extent due to the presence of acid phosphates; to estimate the acidity, the sample is deprived of its carbonic anhydride by means of a strong current of purified air (not by heating at 40—50°), and normal alkali is run in until the sample is neutral to red litmus paper; this will show if there is much free acidity. More alkali is then added until the liquid is neutral to blue litmus paper, which will indicate whether there is much acid phosphate. The free (acetic) acid may be estimated by distilling the sample in a current of steam and estimating

the acidity in the distillate by decinormal alkali. The investigation will be continued.

L. DE K.

Estimation of Tartaric Acid. By L. BRIAND (*Chem. Centr.*, 1897, ii, 919; from *Ann. de Chim. applic.*, 1897, 321).—Fifty c.c. of the filtered wine is mixed with an excess of pure potassium sulphate, well stirred, and after remaining for 2 days in a cool place the liquid is filtered, and the deposit washed with dilute alcohol previously saturated with potassium sulphate and potassium hydrogen tartrate. The estimation is then conducted in the manner directed by Magnier de la Source. The result obtained is corrected by adding 0.35 gram to the weight of the potassium hydrogen tartrate. The process gives, of course, not only the combined, but also the free tartaric acid.

L. DE K.

Analysis of Crude Wine Lees and Argol (*Zeit. anal. Chem.*, 1898, 37, 312—313).—The following mode of procedure, which is employed at the chemical factory "late Goldenberg, Geromont & Co." is recommended; to obtain accurate results it must be followed exactly. Six grams of the finely powdered lees is digested in the cold for 2 hours with 9 c.c. of hydrochloric acid of sp. gr. = 1.1. The mixture is then made up to 100 c.c., vigorously shaken and filtered; 50 c.c. of the filtrate is mixed with 18 c.c. of potassium carbonate solution containing 3.6 grams of the salt, and boiled for 10 minutes; the liquid is then filtered through a suction filter, the insoluble matter washed with boiling water until neutral, and the filtrate evaporated to about 15 c.c., mixed, after cooling, with 3 c.c. of glacial acetic acid, and stirred for 5 minutes. There is now added 100 c.c. of 95 per cent. alcohol, and the mixture is stirred again for 5 minutes, or until the precipitate has become granular. This is now collected on a suction filter and washed with alcohol until free from acid. The precipitate with the filter is thrown into a beaker, into which also the basin is rinsed with 100—120 c.c. of hot water, and is titrated by N/2 potash. For $(20 + n)$ per cent. of tartaric acid thus found $[(20 + n) - (0.7 + 0.02n)]$ per cent. is the true result.

In analysing argol and calcium tartrate, only 3 grams is employed, and the mixture with the hydrochloric acid is made up to 100.5 c.c., 50 c.c. of the filtrate being then treated as above. No correction is applied in these cases.

M. J. S.

Hopkin's Method of Estimating Uric Acid. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1898, 25, 64).—Polemical; a reply to Ritter (this vol., ii, 358).

W. D. H.

Detection of Small Quantities of Cotton-oil in Olive-oil and other Edible Oils. By MASSIMO TORTELLI and R. RUGGERI (*Zeit. angew. Chem.*, 1898, 464—466; and *Gazzetta*, 28, i, 310—321).—The process is based upon the reducing action of cotton-oil on alcoholic silver nitrate, but, instead of applying the test to the original sample, it is applied to the liquid fatty acids obtained by the lead-ether process.

The fatty acids obtained from 5 grams of the sample are thoroughly freed from ether, and then dissolved in 10 c.c. of alcohol containing

1 c.c. of a 5 per cent solution of silver nitrate; the mixture is heated in a water bath to 70—80°, when the presence of cotton-oil is indicated by a more or less pronounced reddish-brown coloration, or even a black deposit. With care, as little as 1 per cent. of adulteration may be detected.

L. DE K.

Analysis of Fats and Resins. By KARL DIETERICH (*Zeit. angew. Chem.*, 1898, 316—318; 434—435).—A controversy with Fahrion on the subject of the analysis of resins and of fats by the fractional saponification process, as to which the author claims priority, and as to the estimation of the acidity figure of fats and resins.

The author estimates this by first adding an excess of standard alkali, and titrating this back with standard acid. The process has nothing in common with Henriques' cold saponification method.

L. DE K.

Analysis of Fats and Resins. By WILHELM FAHRION (*Zeit. angew. Chem.*, 1898, 383—385, 527).—Replies to Dieterich (see preceding abstract). The author was not acquainted with Dieterich's work on the subject of resins. The fractional saponification process was only referred to briefly at the end of the author's paper.

In the second paper, the author replies to Dieterich's second article, and states that his object was to see how far the saponification and similar figures of fats are influenced by the presence of resins.

L. DE K.

Hübl's Iodine Addition Process. By J. J. A. WIJS (*Zeit. angew. Chem.*, 1898, 291—297).—The paper contains an exhaustive investigation into the true nature of the Hübl solution. The author has arrived at the conclusion that when alcoholic solutions of iodine and mercuric chloride are mixed, the liquid contains both mercuric iodide and iodine monochloride; the latter acts on the water, which is always present, forming both hydrochloric and hypoiodic acids. On keeping the solution, the latter acid acts on the alcohol, forming iodine, aldehyde and water.

If the freshly prepared solution is brought into contact with oleic acid, the free acids contained in it so react on the oleic acid as to form water and the chloriodine additive product; this, however, again loses a part of the chlorine as hydrochloric acid.

L. DE K.

Analysis of Soaps. By HURST (*Chem. Centr.*, 1897, ii, 813—814; *Rev. Intern. Falsif.*, 10, 134).—Five grams of the soap is dried at 100°, reweighed, and then treated with light petroleum to dissolve unsaponified fat and free fatty acids; the residue is exhausted with alcohol, the alcoholic solution coloured with phenolphthalein, and any free alkali titrated with normal acid. After diluting with water and expelling the alcohol, the combined alkali is titrated with normal acid in the presence of methyl-orange. The fatty acids are then liberated by boiling with excess of hydrochloric acid, and after drying and weighing they are treated for rosin by Gladding's process. Any glycerol may be recovered by neutralising the acid filtrate with soda,

evaporating to dryness, and extracting with absolute alcohol; the alcoholic extract is evaporated and the glycerol weighed.

L. DE K.

Analysis of Beeswax. By ROBERT HENRIQUES (*Chem. Centr.*, 1897, ii, 647—648; from *Zeit. öffentl. Chem.*, 3, 274—276).—The process is a slight modification of Weinwurm's method; 3 to 4 drops of the melted and clarified sample is boiled for about 4 minutes in a not too narrow test-tube with 5 c.c. of a mixture of 25 c.c. of aqueous soda of sp. gr. = 1.38 and 125 c.c. of glycerol. The wax at first dissolves, but gradually the ley gets turbid, aqueous vapour passing off with much frothing. At a certain moment, the liquid separates sharply into an oily layer and a quite clear liquid, and the glycerol commences to distil. The source of heat is now removed, and the mixture introduced into another test-tube, when it is diluted with an equal bulk of hot water and once more boiled. When cold, the whole forms a jelly which is clear and transparent when the sample is pure, but is quite opaque if more than 5 per cent. of paraffin or ceresin is present. The test fails when the adulteration is only about 3 per cent., and, therefore, it is as well to repeat the experiment after, purposely adding 3 per cent. of ceresin; if a marked opacity is observed, the sample must have contained at least 3 per cent. of the adulterant.

L. DE K.

Estimation of Alkaloids in Pharmaceutical Preparations. By KARL KIPPENBERGER (*Chem. Centr.*, 1897, ii, 646—647; from *Apoth. Zeit.*, 12, 459—460; 467—469).—The extract is dissolved in warm acidified water, filtered if necessary, and precipitated by means of a solution of iodine in a large excess of potassium iodide. The deposit is then repeatedly washed with cold water, preferably on a Gooch's crucible, and after being repeatedly extracted with purified acetone, the latter is diluted with water and shaken with light petroleum first in the presence of alkali and then of acid. The aqueous layer is then warmed to drive off the acetone and traces of light petroleum, and when cold a few drops of N/10 solution of sodium thio-sulphate are added. The liquid is rendered alkaline with sodium carbonate or ammonia and extracted by agitation with chloroform or ether (compare Abstr., 1896, ii, 681—682).

L. DE K.

Behaviour of Codeine and Morphine with Pure Sulphuric Acid. By MICHAÏL P. SERGÉEFF (*Chem. Centr.*, 1897, ii, 664—665; from *Pharm. Zeit. Russ.*, 36, 431—432).—When 1 c.c. of sulphuric acid is poured on to 0.01 gram of codeine, and the mixture viewed by reflected light, purple-violet rings may, after a few minutes, be seen to form round each grain. The coloration appears more quickly on heating, and is then more purple, turning finally to olive-green. When morphine is dissolved in sulphuric acid, the solution is not as clear as that of codeine, and exhibits a brownish-violet coloration, possibly due to partial charring. A saturated solution of morphine hydrochloride in sulphuric acid, after remaining a month, had changed into a gelatinous mass, and still showed the coloration.

E. W. W.

Detection of Aloes. By PIERRE APÉRY (*Zeit. anal. Chem.*, 1898, 37, 276; from *Mitth. Soc. Imp. Med. Constantinople*).—A filtered alcoholic extract of the substance is evaporated to dryness, the residue warmed with water, and the filtered solution precipitated with lead acetate. The lead is removed from the filtrate by boiling with sodium carbonate, and the filtrate is acidified with acetic or nitric acid. A drop of dilute ferric chloride solution gives a distinct reddish-brown coloration when aloes is present to the extent of 1 part in 2000—3000 of water.

Tannin and substances containing phenols, as kola nut, areca nut, &c., also give brownish-red colours with ferric chloride, but since these tonics are usually not simultaneously administered when aloes is given for criminal purposes, and since other drastics, such as savin, absinthin, laxative gum resin, &c., do not give the reaction, the method seems suitable for the chemico-legal detection of aloes.

M. J. S.

Analysis of Commercial Indigo. By C. BRANDT (*Chem. Centr.*, 1897, ii, 813; from *Rev. Intern. Falsif.*, 10, 130—131).—The author substitutes aniline for naphthalene in Schneider's process, as the ethereal solution of the latter deposits solid matter on the filter and so necessitates using large quantities of ether. 0.2 gram of indigo is extracted in a Soxhlet's tube with aniline for about an hour; when cold the indigo will crystallise. Dilute hydrochloric acid is now added to dissolve the aniline as hydrochloride, and the indigotin is then collected on a tared filter and washed first with boiling water and then with alcohol, which at the most dissolves 0.5 per cent. of the total indigotin.

L. DE K.

Detection of Blood. By JESERICH (*Zeit. anal. Chem.*, 1898, 37, 276; from *Pharm. Centr.*, 32, 708).—Photography can be employed to detect blood on steel instruments from which the stains have been wiped, the streaks produced by the wiping being distinctly visible in the photograph.

Amongst mammals, the camel and elephant alone have larger blood corpuscles than man; where these are known to be absent the presence of human blood may be inferred with certainty if the corpuscles have a diameter as great as 0.0078 millimetre.

M. J. S.

General and Physical Chemistry.

Influence of Temperature on the Rotatory Power of Liquids. By PHILIPPE A. GUYE and EMILY ASTON (*Compt. rend.*, 1897, 125, 819—821).—In a former paper (*Abstr.*, 1897, ii, 237), the authors have shown that, in the case of at least fifty optically active liquids, the rotatory power diminishes with a rise of temperature. An apparent exception to this general behaviour in active compounds is afforded by amylic alcohol. The rotatory power of this compound at first diminishes as the temperature rises, but a minimum is reached, and the rotatory power then increases with the temperature, the increase being even maintained in the passage from liquid to vapour. The authors explain this behaviour by pointing out that amylic alcohol is, according to Ramsay and Shields' investigations, an associating liquid, and that the rise of temperature therefore in this case produces a simplification in the molecular structure. That the increase in rotatory power is due to this simplification is shown by the fact that in solution in water, a liquid that effects the dissociation of dissolved substances, amylic alcohol gives a value of $[\alpha]_D = -5.1$, but in solution in benzene, a solvent which has no dissociating properties, the value of $[\alpha]_D$ is only about -4.5 . H. C.

Relations Connecting the Thermal Constants of the Elements. By NOEL DEERR (*Chem. News*, 1897, 76, 234—237).—The empirical relations between the thermal constants of the elements proposed by Pictet, Richards, Crompton, and Deerr are submitted to a critical examination. If T is the absolute melting point, L the latent heat of fusion, C the mean coefficient of expansion, and S the mean specific heat between -273° and T , the relations $TC = \text{const.}$ and $LC/S = \text{const.}$, and from these also $TS/L = \text{const.}$, hold between such elements as bear a close relationship to each other, and hence generally for members of any one periodic group. The other proposed relations are either variations of these, or do not stand the test of a close criticism. The author employs these expressions for the calculation of some undetermined latent heats of fusion. H. C.

Heat of Vaporisation of some Elements and their Molecular Weight in the Liquid State. By ISIDOR TRAUBE (*Ber.*, 1898, 31, 1562—1563).—For the seven elements Br_2 , I_2 , Zn , Cd , Hg , Bi , S_2 (the molecular formulæ in the gaseous state are quoted), the rate of variation of vapour pressure with temperature (in the neighbourhood of the normal pressure), dp/dT , can be calculated from observations, and then, making use of Clausius' formula $\rho = Tdp/dT (V_1 - V_2)$ (where T is the boiling point in absolute temperature, V_1 and V_2 the specific volumes of vapour and liquid at that temperature), it is possible to calculate ρ , the latent heat of vaporisation; this agrees fairly well with that observed.

	Br.	I.	Zn.	Cd.	Hg.	Bi.	S.
Calculated.....	46.7	34.9	390.1	209.6	69.0	201.6	339.9
Observed	43.7	—	—	—	62.0	—	362.0

Substituting these values for ρ in the expression mp/T (where m is the molecular weight in the gaseous state), we ought, according to Trouton's rule, to obtain a number approximating to 20.63 *if the substance have the same molecular weight in the liquid as in the gaseous state*. This is the case (=19.4 to 22.5) with all the above elements except sulphur; for this the value is 30.2. U. F. B.

Calories of Combustion in Oxygen of Cereals and Cereal Products, calculated from Analytical Data. By HARVEY WASHINGTON WILEY and W. D. BIGELOW (*J. Amer. Chem. Soc.*, 1898, 20, 304—316. Compare this vol., ii, 206).—The bomb calorimeter invented by Berthelot and Vieille, in which the substance is burnt in compressed oxygen, has made it possible to determine the calories of combustion of foods with a fair degree of accuracy in agricultural laboratories.

The figure obtained should not differ by more than 75 calories from the result obtained by calculation from the chemical composition of the food; as there is a great difference in the number of calories of the carbohydrates, the proteids and the fatty matters, this is readily done. Should the difference be greater, both the analysis and the combustion in the bomb should be repeated. L. DE K.

Influence of Superfusion on the Freezing Points of Solutions of Potassium Chloride and Sugar. By FRANÇOIS MARIE RAOULT (*Compt. rend.*, 1897, 125, 751—754).—The author has determined the freezing points of aqueous solutions of potassium chloride and cane-sugar, using the same apparatus and precautions which were employed in the determinations with sodium chloride and alcohol (Abstr., 1897, ii, 362). The molecular reduction in the case of potassium chloride increases as the concentration diminishes, and tends to the maximum value 36.4 for infinite dilution. The molecular reduction for cane-sugar diminishes with increasing dilution, and has the limiting value 18.72. The results agree perfectly with those predicted by Arrhenius. H. C.

Compressibility of Gases under Approximately Atmospheric Pressure. By ANATOLE LEDUC and PAUL SACERDOTE (*Compt. rend.*, 1897, 125, 297—299).—In a previous paper (Abstr., 1897, ii, 133), one of the authors has shown that the compressibility of different gases at the same temperature, and approximately under atmospheric pressure, is given by the expression $P_0 V_0 / PV - 1 = A(P - P_0)$. The product $A\pi$ of the coefficient A and the critical pressure π of the gas is a function of the critical temperature θ , so that one and the same function $Z = A\pi = f(\theta)$ should apply to all gases obeying the above law. Eighteen gases were examined, and the values of θ plotted against those of $A\pi$. Fourteen of the points so obtained were found to lie on a regular curve, but the points obtained for the three gases methane, methylic chloride, and ammonia lie well off the curve on the one side, and the point given by hydrogen sulphide lies off the curve on the other side. Regarding the behaviour of the first fourteen gases as normal, the general equation to the curve is $Z = mx^2 - nx^3 + px^4$, in which $x = 175 + \theta$, $m = 135 \times 10^{-5}$, $n = 338 \times 10^{-8}$, $p = 145 \times 10^{-10}$. With the aid of this expression, it is possible to calculate the critical pressure from the known critical

temperature in the case of gases of normal behaviour. The authors have in this way calculated the following critical pressures: acetylene, 67 atm.; hydrogen chloride, 83 atm.; methylic ether, 57 atm.

H. C.

Molecular Volumes and Densities of Gases at all Temperatures and at Mean Pressures. By ANATOLE LEDUC (*Compt. rend.*, 1897, 125, 703—706).—A general expression is obtained for the correction γ , which has to be applied to the observed molecular volume of each gas in order to obtain the molecular volume of the same gas in an ideally perfect state. A close agreement between the calculated and observed values for the densities is obtained in the examples given by the author.

H. C.

Coefficients of Dilatation of Gases at Mean Pressures. By ANATOLE LEDUC (*Compt. rend.*, 1897, 125, 768—770).—The general expression obtained by the author for the densities of gases at different temperatures (see preceding abstract) is utilised for the purpose of calculating the coefficients of dilatation. The calculated and observed values in the examples quoted are in close agreement.

H. C.

Study of Physical and Chemical Equilibria by the Osmotic Method. By A. PONSOT (*Compt. rend.*, 1898, 126, 335—338).—A theoretical paper in which the limitations to the osmotic method of dealing with physical and chemical equilibria are discussed.

H. C.

Rate of Dehydration of Crystallised Salts. By THEODORE WILLIAM RICHARDS (*Zeit. anorg. Chem.*, 1898, 17, 165—169).—The rate at which water is withdrawn from a salt by a dehydrating agent varies greatly for different salts, and for different hydrates of the same salt. In the case of barium chloride, the dehydration takes place rapidly until the point $\text{BaCl}_2 + \text{H}_2\text{O}$ is reached, and then the further dehydration proceeds much more slowly. Most salts which contain a small amount of water of crystallisation behave like barium chloride; but with salts containing a large quantity of water of crystallisation, the curve for the rate of dehydration gives little, or no, indication of the presence of definite hydrates. In order to detect the points at which different hydrates are present and at which a different rate of dehydration commences, it is necessary to employ as the dehydrating agent a substance whose vapour tension is not much less than that of the salt which is being dehydrated. For this purpose, sulphuric acid of various strengths is the most convenient, and the author gives a table of the vapour tension of sulphuric acid of various densities.

E. C. R.

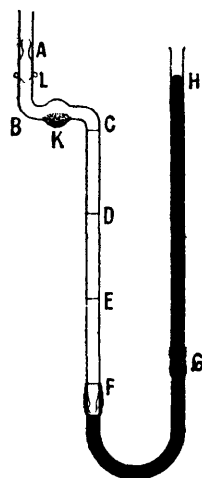
Taste and Affinity of Acids. By J. H. KASTLE (*Amer. Chem. J.*, 1898, 20, 466—471).—The author has carried out a series of experiments with nineteen inorganic and organic acids in order to ascertain whether their degree of sourness could be used to approximately determine their strength. Richards (this vol., ii, 209) has already shown that a qualitative relation exists between the sour taste of acids and their electrolytic dissociation. In the author's experiments, a dilution of N/50 was employed, and over 400 observations were made on 16 individuals of both sexes. About 74 per cent. of the

observations indicated that a definite relation does exist between the taste of acids and their coefficients of affinity.

The author suggests that acidic substances like picric acid and benzoic sulphinide, which are not sour, owe their characteristic taste to the negative ion, since the taste persists in their salts; on the other hand, the sourness of acids which depends on the hydrogen ion, disappears on neutralisation.

G. T. M.

Apparatus for Determining the Composition of Ammonia, Sulphurous Anhydride, Water, &c. By GEORGE GEORGE (*Chem. News*, 1898, 77, 203).—The apparatus consists of a bent tube, AF, of Jena glass of about $\frac{1}{2}$ inch bore, the limbs AB and BC being each about 3 inches long, and CF about 24 inches. The tube is graduated, so that the portions AC, CD, DE, and EF contain equal volumes. To



determine the composition of ammonia, a piece of tubing, provided with a clip, is attached to A, the whole tube filled with mercury by raising the pressure tube, HG, and the dry gas introduced through A. A short thistle funnel is then attached to A, and in it is placed some freshly-ignited copper oxide. By raising the pressure tube and opening the clip, the oxide is made to enter the tube, whilst the escape of ammonia prevents the entry of air. The gas is allowed to escape until AD is just filled at the atmospheric pressure. Sparks are then passed through the electrodes, L, for some time. On cooling and adjusting the pressure, the volume of the gas will have increased to AF (nearly). The copper oxide in the bulb, K, is now heated, and, after the reduction of the oxide by the hydrogen, the volume of the residual nitrogen, after cooling and adjusting the pressure, will occupy AC.

The composition of sulphurous anhydride may be proved by filling the tube with oxygen and burning sulphur in the bulb, that of water by exploding known volumes of oxygen and hydrogen, that of nitrous or of nitric oxide by decomposing the gas with potassium, and that of dry air by means of phosphorus. The apparatus can be obtained from Messrs. Baird and Tatlock.

E. W. W.

Inorganic Chemistry.

Preparation of Graphitic Acid. By LUDWIG STAUDENMAIER (*Ber.*, 1898, 31, 1481—1487).—Graphitic acid may be prepared quite easily in the following manner. One hundred c.c. of concentrated nitric acid (sp. gr. = 1.4) is mixed with 300 c.c. of ordinary strong sulphuric acid in a basin; 50 grams of powdered Ceylon graphite (or,

still better, commercial "Graph. ceylon. alcohol") is added to the cold mixture, and then 100 grams of potassium chlorate, in portions, at short intervals and with frequent stirring; after the whole has remained for several hours, it is poured into water, the solid is washed, dried, and ignited in a large metal dish until it has intumesced; finally, it is stirred with water, and the part that floats is used for further operations. Twenty-five grams of this prepared graphite is stirred into a cold mixture of 1 litre of strong sulphuric acid with $\frac{1}{2}$ litre of strong nitric acid contained in a shallow basin, and then about 450 grams of potassium chlorate is added in portions at intervals; when the vigorous evolution of gas has slackened, and a small sample of the green solid is found to be pure yellow after treatment with acid permanganate, the whole is poured into water, and the solid is washed repeatedly by decantation (the gelatinous particles that obstinately refuse to settle may be poured away, as their weight is relatively very small); it is now brought into a basin, and to it is added a solution prepared by dissolving 7 grams of potassium permanganate in 120 c.c. of hot water, cooling, and adding a mixture of 15 c.c. of strong sulphuric acid and 75 c.c. of water; the whole is then heated on the water bath until the red colour has disappeared, hydrogen peroxide is added (or hydrochloric acid, with or without alcohol), the whole is allowed to remain for a time, being stirred occasionally, and the solid graphitic acid is then washed with dilute nitric acid (sp. gr. 1.28), and, finally, with alcohol and ether.

The operation lasts only 1—2 days, and in the winter-time, with the temperature little above 0° , 50—100 grams of graphite might be oxidised at once without risk of dangerous explosions. A specimen may be prepared in a couple of hours on quite a small scale by stirring 30 grams of chlorate into a mixture of 40 c.c. sulphuric and 20 c.c. nitric acids at 20° , adding 1 gram of prepared graphite, and proceeding to the final oxidation with permanganate after an hour or so.

C. F. B.

Oxidation of Sodium Sulphide by Electrolysis. By AUGUSTE SCHEURER-KESTNER (*Bull. Soc. Chim.*, 1897, [iii], 17, 99—100. Compare Abstr., 1896, ii, 559).—The author contends, in opposition to Durkee, that sodium sulphide, on electrolysis, is oxidised directly to sodium sulphate, without the intermediate formation of thiosulphate.

N. L.

Solubility of Calcium and Magnesium Hydrogen Carbonates. By FREDERICK PEARSON TREADWELL and M. REUTER (*Zeit. anorg. Chem.*, 1898, 17, 170—204).—Calcium hydrogen carbonate is present as such in an aqueous solution prepared by saturating a solution of lime with carbonic anhydride, and then allowing the free carbonic anhydride to escape at 15° and 760 mm. pressure. One litre of water dissolves 0.3850 gram of calcium hydrogen carbonate. The paper contains tables and curves of the solubility of calcium hydrogen carbonate in water containing carbonic acid, showing the solubility as a function of the partial pressure of the carbonic acid and as a function of the free carbonic acid dissolved in the water. The solubility of calcium hydrogen carbonate is not increased by the presence of sodium chloride.

Magnesium hydrogen carbonate is not stable except in the presence of free carbonic acid. At 15° and 760 mm., a solution having the partial pressure of the carbonic anhydride ≈ 0 contains 1.9540 grams of hydrogen carbonate and 0.7156 gram carbonate in 1 litre.

Experiments with solutions of sodium hydrogen carbonate show that they gradually decompose after a time. E. C. R.

Action of Zinc on Copper Silicide. By GUILLAME J. L. DE CHALMOT (*Amer. Chem. J.*, 1898, 20, 437—444).—The author finds that zinc decomposes copper silicide, liberating silicon, whilst tin and antimony do not affect this compound. The silicide employed in the experiments consisted of 50—52 per cent. of Cu_2Si , free copper, and a small amount of iron silicide; the zinc used contained only traces of iron and carbon. The silicide was first melted, and the molten zinc then added; the silicon liberated was always crystalline. Experiments made with varying quantities of zinc showed that practically no silicon was liberated until the quantity of zinc present was in excess of that required to form the compound ZnCu_2 with the free copper. Above this limit, the quantity of silicon liberated increased as the excess of zinc became greater, until when the ratio of copper to zinc was 100 to 195, about 95 per cent. of the total silicon was in the free state.

G. T. M.

Metallic Phosphides. By ALBERT GRANGER (*Chem. News*, 1898, 77, 227—229; from *Mon. Sci.*, [iv], 12, May, 1898).—Largely a résumé of work previously published (see Abstr., 1895, ii, 392; 1896, ii, 365, 476, 602, 650; 1897, ii, 215, 265, 323, 371, 453).—The author has examined the various methods of preparing metallic phosphides, and described a number of these compounds. When phosphides are prepared by passing an inert gas containing phosphorus vapour over a heated metal, the product should be cooled in an atmosphere of phosphorus in order to prevent dissociation. With metals, phosphorus is capable of forming substances similar to alloys, which often have the appearance of compounds, and sometimes are crystalline; such are the alloys Cu_3P and Fe_4P of Abel and Sidot; the former yields a definite compound, Cu_5P_2 , by the prolonged action of phosphorus, and the latter may be obtained, with other more or less dephosphorised products, by heating iron subphosphide for a long time. By the action of phosphorus trichloride on metallic iron, and by heating ferric chloride in the vapour of phosphorus, the author has prepared Fe_4P_3 and Fe_2P_3 respectively; these phosphides crystallise in white, prismatic needles, and are not easily attacked except by chlorine. Pure crystalline cuprous phosphide can be obtained by allowing phosphorus to remain with copper phosphite under water. Manganese phosphide, Mn_3P_2 , is formed in thin, brilliant plates by heating the chloride in a current of the vapour of phosphorus in hydrogen. When phosphorus di-iodide is heated with mercury, the phosphide Hg_3P_4 is obtained in hexagonal prisms; it is easily decomposed by heat. Silver or silver chloride, when heated in the vapour of phosphorus at 400° , forms a diphosphide which decomposes at 500° , and under similar conditions gold yields a phosphide, Au_3P_4 , which is easily decomposed by heat. Platinum, when heated with phosphorus, forms easily fusible com-

pounds; at 500° , the diphosphide is obtained; at about 600° , the phosphide Pt_3P_5 ; above 700° , a subphosphide; at 1000° , only a very small percentage of phosphorus is retained by the metal. Lead, bismuth, and antimony do not combine with phosphorus directly.

E. W. W.

Atomic Weight of Nickel and Cobalt. By CLEMENS WINKLER (*Zeit. anorg. Chem.*, 1898, 17, 236—240).—The author compares the method employed by himself with that employed by Richards and Cushman and Richards and Bunter (this vol. ii, 228, 377). He maintains that his method is most accurate, and points out that the dry bromide obtained in Richards' method most probably contains a trace of hydrogen bromide.

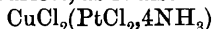
E. C. R.

Action of Nitric Acid on Tin in Presence of Metals of the Iron Group. By FREDERIK HENDRIK VAN LEENT (*Rec. Trav. Chim.*, 1898, 17, 86—93).—When tin is dissolved in nitric acid in presence of one-fifth or one-sixth of its weight of iron, and the solution evaporated to dryness, a product completely soluble in water is obtained; on adding concentrated nitric acid to the aqueous solution, a precipitate is obtained containing the whole of the tin, and a considerable proportion of iron which it is impossible to remove. When dried by exposure during several weeks in a vacuum over caustic potash, the product gradually loses water and nitric acid; analyses show that there is no constant relation between the amounts of iron and nitric acid present. The dried product dissolves in water, giving a solution from which metastannic acid is precipitated by an excess of hydrochloric acid; on subsequently boiling, the precipitate dissolves, and on adding caesium or rubidium chloride, characteristic crystals of caesium or rubidium chlorostannate are obtained. When, however, a small quantity only of hydrochloric acid is added to the original aqueous solution no precipitate is formed, and on adding caesium or rubidium chloride an amorphous precipitate is obtained. By these tests, the two varieties of stannic acid are distinguished (compare Behrens, *Anal. qual. microchim.*, 63).

The author finds that the nitrates of chromium and aluminium exercise the same power of rendering metastannic acid soluble as ferric nitrate, whilst this is not the case with the nitrates of nickel, cobalt, and manganese.

W. A. D.

Relation between the Colour and the Constitution of Haloid Double Salts. By NICOLAI S. KURNAKOFF (*Zeit. anorg. Chem.*, 1898, 17, 207—235).—Compounds of the type $\text{MCl}_2, \text{PtCl}_2, 4\text{NH}_3$ exist in two isomeric forms of which those which may be represented by the formula $(\text{MCl}_2, 4\text{NH}_3), \text{PtCl}_2$, are characterised by their red to violet-red colour, whilst the isomeric compounds, $\text{MCl}_2(\text{PtCl}_2, 4\text{NH}_3)$, have the same colour as the corresponding anhydrous metallic chlorides, or as the analogous anhydrous double salt; for example, $\text{ZnCl}_2(\text{PtCl}_2, 4\text{NH}_3)$ is colourless, as is also ZnCl_4K_2 , whilst



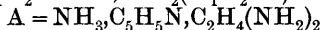
and CuCl_4R_2 ($\text{R} = \text{Cs}, \text{NMe}_4$) are both brownish-yellow. The corresponding palladium compound, $\text{CuCl}_2(\text{PdCl}_2, 4\text{NH}_3)$, also crystallises in dark

yellow tablets; it is obtained by mixing solutions of copper chloride and $\text{PtCl}_2 \cdot 4\text{NH}_3$, and is decomposed by excess of water and hydrochloric acid.

The alteration of colour by the introduction of water, ammonia, or its derivatives into inorganic salts is analogous to that which takes place by the introduction of bathochromic groups into organic compounds. Thus PdCl_2 is reddish-brown; $\text{PdCl}_2 \cdot 2\text{NH}_3$, yellow; and $\text{PdCl}_2 \cdot 4\text{NH}_3$, colourless; $\text{CoCl}_2 \cdot 4\text{NH}_3$ (praseo-salt) is green; $\text{CoCl}_2 \cdot 5\text{NH}_3$ (purpureo-salt), red; and $\text{CoCl}_2 \cdot 6\text{NH}_3$ (luteo-salt), yellow.

In the formation of double salts, the colour is generally produced by the addition of the colours of the components; thus the violet salt, $(\text{CuCl}_2 \cdot 4\text{NH}_3) \cdot \text{PtCl}_2$, is produced from the green salt, $\text{CuCl}_2 \cdot 4\text{NH}_3$, and the red chloroplatinite. The coloration of double salts is not, however, very regular. A deepening of the colour often takes place whereby yellow salts are formed from colourless constituents, or dark red salts from brown, as in the double compounds of CuBr_2 with KBr and HBr .

The author has examined the cobalt and copper compounds of the types I, $(\text{MX}_2 \cdot n\text{A})\text{M}_1\text{X}_2$ and II, $\text{MX}_2(\text{M}_1\text{X}_2 \cdot n\text{A})$ where



and H_2O .

In series I, the colour of the compound is normal as regards the metal M, that is, the normal colour of the component $\text{MCl}_2 \cdot n\text{A}$ is a component of the colour of the double salt. In series II, the colour of the compound is abnormal as regards the metal M, that is, the component MCl_2 , in so far as colour is concerned, behaves as if anhydrous.

The author proposes to name compounds of the type $\text{MX}_2(\text{M}_1\text{X}_2 \cdot n\text{A})$ *chlorometallites*, in accordance with the name chloroplatinites, thus $\text{CuCl}_2(\text{PtCl}_2 \cdot 4\text{NH}_3)$ and $\text{CoCl}_2(\text{PtCl}_2 \cdot 4\text{NH}_3)$ he names platodiammine chlorocuprite and platodiammine chlorocobaltite.

Chlorocobaltites.—The difference in the colour of anhydrous cobalt chloride, and of its compounds with water and ammonia, is also apparent in the corresponding double salts. When cobalt chloride is combined with colourless ammonium, pyridine, and ethylenediammine salts of the type $\text{PtCl}_2 \cdot 4\text{A}$, a series of salts of the formula $\text{CoCl}_2(\text{PtCl}_2 \cdot 4\text{A})$ is obtained which have the blue colour of cobalt chloride.

Platodiammine chlorocobaltite, $\text{CoCl}_2(\text{PtCl}_2 \cdot 4\text{NH}_3)$, obtained by adding finely powdered platodiammine chloride to a boiling saturated solution of cobalt chloride, crystallises in transparent, blue, rhomboidal tablets, decomposes into its components when dissolved in water, and yields a red solution with excess of water. The corresponding *pyridine* compound, $\text{CoCl}_2(\text{PtCl}_2 \cdot 4\text{C}_5\text{H}_5\text{N})$, crystallises in small, thin tablets, and is very easily decomposed into its components. The *ethylenediammine* compound crystallises in beautiful, blue prisms, is very stable, and can be warmed with hydrochloric acid for some time without decomposition.

The relation of the colour of the chlorometallites to the colour of their anhydrous components is also shown in the compounds of cobalt and copper chloride with ethylenediammine hydrochloride. The *cobalt* compound, $\text{CoCl}_2(\text{C}_2\text{H}_5\text{N}_2 \cdot 2\text{HCl})$, crystallises in large, blue tablets. The *copper* compound crystallises in brownish-yellow, quadratic tablets.

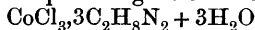
Chloroplatinites.—The salt, $\text{PtCl}_2(\text{CoCl}_2, 6\text{NH}_3)$, obtained by adding a solution of potassium platinochloride to an ammoniacal solution of cobalt chloride in an atmosphere of hydrogen or nitrogen, crystallises in thin, yellowish-red, right-angled tablets, is decomposed by water with the formation of an insoluble basic compound, and yields a blue solution with hydrochloric acid; it is stable when dry, but when allowed to remain for some time over sulphuric acid it loses ammonia and is converted into a mixture of the salts, $\text{PtCl}_2(\text{CoCl}_2, 6\text{NH}_3)$ and $\text{PtCl}_2(\text{CoCl}_2, 4\text{NH}_3)$. The ammonia in this double salt is evidently more firmly combined than in the salt $\text{CoCl}_2, 6\text{NH}_3$, which at the ordinary temperature rapidly gives off ammonia when allowed to remain over sulphuric acid. The corresponding *nickel* salt, $\text{PtCl}_2(\text{NiCl}_2, 6\text{NH}_3)$, which is obtained in a similar manner, crystallises in rose-red, four-sided tablets having a violet tinge.

The compounds obtained by the action of potassium platinochloride on solutions of silver chloride in ammonia and ethylenediammine, are of a higher type as regards their capability of retaining ammonia than the compounds of silver chloride with ammonia and ethylenediammine. Freshly prepared silver chloride, when dissolved in a warm aqueous solution of ethylenediammine, yields the compound $(\text{AgCl})_2\text{C}_2\text{H}_8\text{N}_2$, which is decomposed by water and alcohol with precipitation of silver chloride. When, however, the solution of silver chloride in ethylenediammine is treated with potassium platinochloride, the compound $(\text{AgCl}, \text{C}_2\text{H}_8\text{N}_2), \text{PtCl}_2$ is obtained, which crystallises in microscopic, bright red tablets.

The chlorocuprite, $\text{CuCl}_2(\text{PCl}_2, 4\text{C}_5\text{NH}_5, 6\text{H}_2\text{O})_2$, is obtained in yellow tablets by concentrating a mixed solution of copper chloride and platodipyridine chloride. A salt of the composition $(\text{PtCl}_2, 4\text{C}_5\text{NH}_5)_2\text{CuCl}_2$ is obtained from the mother liquor of the preceding salt and crystallises in reddish-brown, rhomboidal tablets.

The *chlorocobaltite*, $\text{CoCl}_2(\text{CoCl}_3, 3\text{C}_2\text{H}_8\text{N}_2 + n\text{H}_2\text{O})$, is obtained by evaporating a solution of $\text{CoCl}_3, 3\text{C}_2\text{H}_8\text{N}_2 + 3\text{H}_2\text{O}$ and $\text{CoCl}_2 + 6\text{H}_2\text{O}$, and crystallises in dark green needles; it is easily decomposed by water with precipitation of the salt, $\text{CoCl}_3, 3\text{C}_2\text{H}_8\text{N}_2 + 3\text{H}_2\text{O}$, but can be washed with concentrated hydrochloric acid without appreciable decomposition. When dehydrated in a desiccator or at $100-115^\circ$, it does not alter in appearance, the dehydration commences with great ease at ordinary temperatures, but the last 1—2 molecules are not lost even at $110-115^\circ$. The determination of the water of crystallisation gave numbers agreeing with 5 to $7.5\text{H}_2\text{O}$.

The *chlorocuprite*, $\text{CuCl}_2(\text{CoCl}_3, 3\text{C}_2\text{H}_8\text{N}_2 + \text{H}_2\text{O})$, is obtained by evaporating a solution of equal weights of $\text{CuCl}_2 + 2\text{H}_2\text{O}$ and



in large, yellowish-brown tablets; it is only sparingly soluble in the presence of hydrochloric acid, and does not lose water when allowed to remain over sulphuric acid, but is completely dehydrated at 112° . The salt, $\text{CuCl}_2(\text{CoCl}_3, 3\text{C}_2\text{H}_8\text{N}_2 + \text{H}_2\text{O})_2$, is obtained by evaporating a solution of molecular proportions of CuCl_2 and $\text{CoCl}_3, 3\text{C}_2\text{H}_8\text{N}_2$, and crystallises in prisms of the same colour as the preceding salt.

A *chlorocuprite* of the composition $(\text{CuCl}_4, \text{Pt}_2\text{C}_2\text{H}_8\text{N}_2)_3, \text{PtCl}_4, 2\text{C}_2\text{H}_8\text{N}_2 + 9\text{H}_2\text{O}$, obtained by the action of platoethylenediammine chloride on

copper chloride, crystallises in greenish-brown, prismatic needles. The corresponding bromide crystallises in dark brown needles. Both salts when dehydrated do not alter in appearance. E. C. R.

Mineralogical Chemistry.

Tellurium in the Product of the Eruption of the Island of Vulcano, Lipari Isles. By ALFONSO COSSA (*Zeit. anorg. Chem.*, 1898, 17, 205—206).—Tellurium is present to the extent of 2 grams in 3 kilograms in the stalactiform concretions occurring largely in the crater of Vulcano (Abstr., 1878, 952; 1882, 704). The product of eruption is extracted with water, then with carbon bisulphide, and finally with dilute nitric acid. The acid solution is treated with hydrogen sulphide, which precipitates the tellurium together with a large quantity of sulphide of arsenic and metallic sulphides.

E. C. R.

Argon in the Vöslau Springs (Vienna). By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1898, 19, 114, 115).—The authors find that the gases from the Vöslau springs contain from 1.29—1.38 per cent. of argon.

A. W. C.

New Experiments on Zeolites. By GEORGES FRIEDEL (*Zeits. Kryst. Min.*, 1898, 29, 278—279; from *Bull. Soc. fran. Min.*, 1896, 19, 363—390. Compare Abstr., 1896, ii, 481, 482).—The amount of water given off by analcite at a definite temperature is dependent on the tension of aqueous vapour in the air; it is therefore necessary, when determining the amount of water lost on heating zeolites, to observe the tension of aqueous vapour as well as the temperature. Constant results are only obtained when the powdered mineral is heated in a rapid current of dry air. If, after dry air has been used, a current of moist air be passed over the heated mineral, there is, in spite of the elevated temperature, an absorption of water, and to expel this again with the same tension of aqueous vapour, a higher temperature is required. Equilibrium in such cases is more rapidly established the higher the temperature; that is, water is more slowly re-absorbed the lower the temperature.

More accurate determinations of the sp. gr. and contraction in volume of partially dehydrated analcite have been made. The contraction continues after all the water has been expelled, the material being then transparent and isotropic, and with numerous microscopic cavities. The optical behaviour of a plate parallel to a cube face when heated is described. Analcite is considered to be tetragonal (pseudo-cubic) like leucite.

L. J. S.

Physiological Chemistry.

Absorption of Fat. By R. H. CUNNINGHAM (*J. Physiol.*, 1898, 23, 209—216).—After ligation of both biliary and pancreatic ducts, some absorption of fat, other than the naturally emulsified fat of milk, still occurs. The rate of absorption is slow, and the quantity absorbed small, but otherwise the process does not differ from that which occurs normally, when both bile and pancreatic juice are present. The experiments were made on dogs. W. D. H.

Metabolism of Nucleins. By T. H. MILROY and J. MALCOLM (*J. Physiol.*, 1898, 23, 217—239).—The digestive products of nuclein-containing tissues, nucleins, and especially nucleic acid, cause, on absorption, a temporary leucocytosis, accompanied by an increase in the excretion of phosphoric anhydride, beyond that which can be explained by the phosphorus absorbed. The alloxuric substances are also increased, whilst the uric acid is only slightly increased, but the experiments being made on human beings, only small doses of nucleic acid were administered, unpleasant symptoms being caused by large doses. Metaphosphoric acid produces none of these results.

The leucocytosis is followed by leucolysis, and this is considered to be the cause of the increase in the urinary phosphates. In a case of leucocythæmia, leucolysis did not occur, and increase in the phosphates excreted was not observed either; the alloxuric substances including uric acid were, however, increased in this case.

In a case of plumbism, the conditions are comparable with those existing normally in spite of the leucocytosis, which was not, however, very marked.

In all cases, uric acid was absent in the fæces.

W. D. H.

Osmotic Properties of Frog's Muscle. By ELIZABETH COOKE (*J. Physiol.*, 1898, 23, 137—149).—A muscle immersed in a hypertonic solution of sodium chloride does not behave according to the laws of osmotic pressure, but owing doubtless to decomposition processes consequent on its taking up water, the muscle behaves like a solution having a higher osmotic pressure than the solution for which it is isotonic. Rise of temperature and fatigue increases the osmotic pressure within the muscle. W. D. H.

Action of Cobra Venom and Calmette's 'Anti-venomous Serum' on Blood Clotting. By J. W. W. STEPHENS and W. MYERS (*Proc. Physiol. Soc.*, May, 1898, 1).—Cobra venom delays or prevents the clotting of rabbits' blood; this effect is neutralised *in vitro* by Calmette's anti-venomous serum. The neutralisation of the toxin by the anti-toxin must be chemical, not vital or cellular as Calmette considers. The blood of a rabbit, immunised with injections of cobra-poison, so far as clotting is concerned, has also acquired a certain amount of immunity against cobra poison. W. D. H.

Chemistry and Action of the Thyroid Gland. By ROBERT HUTCHISON (*J. Physiol.*, 1898, 23, 178—189).—The iodine contained in the colloid matter of the thyroid varies considerably, and averages 0.309 per cent. Of the digestion product of the colloid, only those which contain iodine are active. Iodised nucleo-albumin, made artificially from the thymus, has no physiological activity, and increase in activity of the thyroid colloid is not produced by artificial addition of iodine, although in the natural products the amount of iodine and the activity vary directly. Intravenous injection of the colloid has no effect on blood pressure, heart, or coagulation of the blood. Thyroid extracts produce a fall of arterial pressure, but this is due to extrac-tives and partly to mineral salts present.

Previous removal of ovaries or testes has no influence on the results of thyroidectomy, and ovarian feeding has no curative influence in myxœdema. No poison was discovered either in the bile or the central nervous system after thyroidectomy.

Of 24 consecutive cases of complete thyroidectomy, only four survived; this number can only be slightly increased by thyroid feeding. Parathyroid feeding has no effect in myxœdema. Keeping the animals warm after the operation has no effect.

W. D. H.

Changes in the Urine produced by Exercise and by Turkish Baths. By G. C. GARRATT (*J. Physiol.*, 1898, 23, 150—162).—Rapid but not laborious exercise (on a bicycle) produces an increase in urea excretion, reaching a maximum in 12 hours but not regaining the normal level for 30 hours afterwards, the increase beginning immediately after the exercise. The excretion of uric acid rises to the maximum six hours after the exercise. If the subject is not in good condition or the food insufficient, the rise is greater and lasts longer. There is an increase in the acidity after exercise which runs parallel to the urea, and a small increase in the urinary phosphates which follows the same course. The increase in the sulphates is proportional to that of the urea, but is of less duration and therefore of more intensity; it begins during the exercise, reaches a maximum in six hours or less, and terminates within 12 or 14 hours. The chlorides of the urine diminish and vary with the amount of sweating. Turkish baths produce a reduction in the water and in the chlorides excreted by the kidneys.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation without Yeast Cells. VII. Preparation of Dried Yeast Juice. By EDUARD BUCHNER and RUDOLF RAFF (*Ber.*, 1898, 31, 1531—1533).—Five hundred c.c. of freshly expressed yeast juice is mixed with a few drops of olive oil, and evaporated rapidly under diminished pressure at 20—25° to a syrupy consistency; this requires about half-an-hour. The syrup is then spread on glass plates cleaned with ether, and dried for about a day, either under

diminished pressure at 35°, or in the air at 34—38°, or at 25°; the residue is then scraped off and dried further over sulphuric acid, preferably under diminished pressure. In this way, 70 grams of a yellowish powder, resembling dried egg-albumen in appearance, is obtained; it has a pleasant odour of yeast, and it dissolves almost completely in water; the solution, when diluted to the original volume, has nearly the same power of inducing fermentation as the original juice.

C. F. B.

Alcoholic Enzyme from Yeast-cells. By CHARLES JAMES MARTIN and H. G. CHAPMAN (*Proc. physiol. Soc.*, June, 1898, 2).—An endeavour to procure a soluble alcoholic ferment from active yeast cells was unsuccessful. The procedure adopted varied from that used by Buchner in the omission of great pressure, centrifugal force being relied on to extract the ferment from the yeast which had been previously ground up with sand and siliceous earth.

W. D. H.

Decomposition of Proteids and the Formation of Asparagine and Glutamine in Seedlings. By ERNST SCHULZE (*Chem. Zeit.*, 1897, 21, 625—628. Compare *ibid.*, 1896, 20, 143; Abstr., 1897, ii, 156; and this vol., ii, 133).—The results of the author's experiments leave it undecided as to the manner in which asparagine and argenine are produced from other products of the decomposition of proteids, but there can be no doubt that both amides can be produced in the plant from ammonia (Suzuki, Abstr., 1897, ii, 277), and if it is admitted that ammonia (which has been detected in seedlings) is formed during the decomposition of proteids, the synthesis of the amides can be explained in this way. The substances formed when the proteids break up are in part utilised in the regeneration of proteids, some being so utilised to a much greater extent than others. It is suggested that the latter decompose further, and that the nitrogenous residue, perhaps ammonia, is used up in the production of the amides, the accumulation of which would be thus accounted for. It is, however, not impossible that a certain amount of asparagine may be formed directly in the decomposition of proteids.

The decomposition of proteids in seedlings consists in the hydrolytic breaking up of the proteid-molecule, and is, perhaps, similar to what takes place in the animal organism (compare Drechsel, Abstr., 1892, 515). Not only in animals, but probably in plants also, the sulphur of the proteids is finally converted into sulphates (compare *Landw. Versuchs.-Stat.*, 1876, 19, 172). This lends support to the view that in plants, as in animals, the (non-nitrogenous) products of the breaking up of proteids undergo oxidation, and, in a certain sense, justifies the assumption of a connection between production of asparagine and the oxidation of proteids (Palladin, Abstr., 1888, 642; compare also Boussingault, *Compt. rend.*, 1864, 58, 921—922).

N. H. J. M.

Analytical Chemistry.

Micro-chemical Detection of Perchlorates in Chili Saltpetre. By M. VAN BREUKELEVEEN (*Rec. Trav. Chim.*, 1898, 17, 94—95).—Behrens' method of testing a solution for perchlorates consists in adding to a drop of the latter on a microscope-slide a small quantity of rubidium chloride; rhombic crystals immediately separate, which are stained red by the addition of a drop of potassium permanganate solution, the latter being rendered colourless. This test gives satisfactory results with aqueous solutions containing more than 0.001 gram of potassium perchlorate per c.c.; but its sensitiveness is diminished by the presence of sodium nitrate, so that it just ceases to be available when 5 grams of Chili saltpetre containing 0.6 per cent. of perchlorate is dissolved in 10 c.c. of water. If the nitrate contains more than 0.6 per cent. of perchlorate, the amount of the latter can be determined approximately by carefully diluting until the limit of sensibility of the test is reached. When the perchlorate forms only 0.2—0.6 per cent. of the nitrate, its presence can be detected by dissolving 10 grams of the latter in 10 c.c. of warm water, adding 50 c.c. of 95 per cent. alcohol, boiling, and leaving to crystallise during 2 hours; on filtering, evaporating to dryness, and dissolving the residue in the least possible quantity of water, a solution is obtained which can be tested by Behrens' method.

W. A. D.

Gladding's Method for [the Estimation of] Phosphoric Acid. By JOHN B. COPPOCK (*Chem. News*, 1898, 77, 242).—The author finds that, whilst Gladding's method of estimating phosphoric acid (this vol., ii, 405) gives higher results than the magnesia method, it affords a quick and sufficiently accurate process for the ordinary analysis of fertilisers.

E. W. W.

Estimation of Phosphorus and Sulphur in Iron, Steel, and Cast Iron. By MAURICE LUCAS (*Bull. Soc. Chim.*, 1897, [iii], 17, 144—150).—Comparative analyses have been made by a number of well-known methods, and the results obtained are exhibited in a tabular form. The chief conclusions arrived at are as follows.

The results given by those methods in which phosphoric acid is precipitated by ammonium molybdate in presence of hydrochloric acid, or of chlorides, are too low; nitric and sulphuric acids, on the other hand, appear to be without influence in this respect. A common source of error lies in the insufficient quantity of molybdate employed. For every 2 parts of iron in solution 3 parts of molybdic acid are required, whilst it is also indispensable that ammonium salts should be present, and that the temperature should be raised to 80°. In the precipitation of phosphoric acid along with basic acetate of iron, a process which is convenient when arsenic is present, it is necessary to precipitate three or four times as much iron as is required to combine with the phosphoric acid, and to remove all acids but nitric before adding the ammonium molybdate.

The whole of the sulphur contained in the metal is expelled as hydrogen sulphide when hydrochloric acid, or a mixture of the latter with sulphuric acid, is used as the solvent, the gases evolved being afterwards passed through a red-hot tube. Low results are obtained when sulphuric acid alone is employed. Of the various methods of estimating the hydrogen sulphide thus produced, the best results are obtained (a) by converting it into sulphuric acid and then into barium sulphate, (b) by iodometric titration, and (c) by the author's colorimetric process (this vol., ii, 483). N. L.

Application of the Colorimetric Method for Estimating Lead to the Estimation of Sulphur in Iron, Steel, and Cast Iron. By MAURICE LUCAS (*Bull. Soc. Chim.*, 1897, [iii], 17, 150—152).—The metal is heated in a current of hydrogen with a mixture of dilute hydrochloric and sulphuric acids, the gases evolved being passed through a red-hot porcelain tube, and finally received in a solution of lead oxide in caustic potash. The precipitated lead sulphide is filtered off, washed with water, dilute acetic acid, and then again with water, dissolved in nitric acid, the solution neutralised with caustic soda, suitably diluted, and examined colorimetrically according to the author's process for the estimation of lead (*Abstr.*, 1897, ii, 125). N. L.

Sodium Peroxide in Quantitative Analysis. By CHARLES GLASER (*J. Amer. Chem. Soc.*, 1898, 20, 130—133).—A review of various propositions made since 1892 regarding the use of sodium peroxide as an oxidising agent either in the dry or in the wet way.

The reagent may be obtained perfectly free from iron, alumina, &c., and is the best oxidising agent for the estimation of sulphur in coal, coke, or asphalt.

The material is placed in a large silver or nickel dish, covered with four times its weight of dry sodium carbonate, and upon this is laid a piece of sodium peroxide about one-half the weight of the carbonate used. The dish is now moved carefully and slowly over a small flame until the evolution of gas subsides and a half-fused mass is obtained. Small quantities of powdered peroxide are now dusted in the mass from a platinum spoon from time to time until all the carbon has burnt away, when, if necessary, the heat may be raised until the mass is in perfect fusion. The sulphur is thus converted into sulphuric acid, which is then estimated as usual.

The author cannot recommend the reagent for chrome ore analysis.

L. DE K.

Estimation of Boric Acid. By THOMAS S. GLADDING (*J. Amer. Chem. Soc.*, 1898, 20, 288—289).—The apparatus consists of a round-bottomed distilling flask placed in a slanting position. It is fitted with a doubly perforated cork, through which pass two bent glass tubes, one of which reaches to the bottom of the flask and is also connected with a larger flask in which methylic alcohol is being boiled; the second, or outlet, tube is connected with a condenser, and the distillate is collected in a Volhard's nitrogen bulb apparatus.

Into the distilling flask, which holds 150 c.c., 1 gram of the

borate is introduced and also 25 c.c. of methylic alcohol and 5 c.c. of syrupy phosphoric acid; a current of methylic alcohol vapour is then passed in, and heat is also applied to prevent accumulation of liquid in the flask. After half an hour's action, when the distillate will measure about 100 c.c., the distillation is stopped and the distillate which now contains all the boric acid is mixed with 100 c.c. of water and 40 c.c. of glycerol, and titrated with standard soda, using phenolphthalein as indicator. The test-analyses are very satisfactory.

It has been noticed that ordinary borax, when distilled with methylic alcohol without the addition of an acid, gives up one-half of its boric acid.

L. DE K.

Kopfer's Method for the Estimation of Carbon and Hydrogen.

By JAMES JOHNSTONE DOBBIE and ALEXANDER LAUDER (*Chem. News*, 1898, **77**, 215—216).—According to the authors, Kopfer's method of estimating carbon and hydrogen by combustion in oxygen in the presence of platinised asbestos (this *Journal*, 1876, **i**, 660; 1877, **i**, 228) is inapplicable to the case of volatile substances, the difficulty of regulating the combustion so as to prevent the escape of unoxidised material being insuperable. Moreover, the results obtained with alkaloids containing large percentages of carbon and little nitrogen, such as cinchonine and corybulbine were invariably too low (compare Zeisel, *Monatshefte*, 1886, **7**, 557).

E. W. W.

The Moist Combustion Method of Determining Carbon in Steel. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1898, **20**, 243—253).—This is an elaborate investigation into the sources of error in the estimation of carbon by the moist combustion process.

The potash solution used to absorb the carbonic anhydride should have a sp. gr. = 1.4 and two absorbing apparatus should be used. The calcium chloride used for drying the gases should be freshly heated. The author also states that, notwithstanding all the usual precautions, results are occasionally obtained by this process which are decidedly too high; this may be explained by the formation of some volatile chlorochromic compound not absorbed by Langley's "pyro" mixture.

L. DE K.

Lindo-Gladding Method of Estimating Potash. By A. L. WINTON and HOMER J. WHEELER (*Chem. News*, 1898, **77**, 263—265, 275—276).—The results of an examination of the Lindo-Gladding method of estimating potash, especially in reference to the objections of Breyer and Schweitzer, and of Vogel and Haefcke, that the addition of sodium chloride is liable to prove a source of error, and that potassium platinochloride is soluble in ammonium chloride solution, have proved these objections to be unfounded, in so far as practical considerations go.

E. W. W.

Alkalimetric Estimation of Metals. By HENRI LESCŒUR (*Bull. Soc. Chim.*, 1897, [iii], **17**, 119—126; 126—132; 132—139; 140—144. Compare this vol., **ii**, 455).—*Estimation of Aluminium.*—Satisfactory results may be obtained by the direct titration of dilute solutions of potassium alum with caustic soda or baryta water, using phenolphthalein

as indicator, but it is better to boil with a known excess of alkali and titrate back with acid. When free acid is present, this is first neutralised by the addition of alkali until the end-point indicated by helianthin is reached; phenolphthalein is then added, and the aluminium titrated as above described. Alumina may also be precipitated by ammonia in the cold, and the washed precipitate dissolved in standard acid and titrated back with alkali, using helianthin as indicator. The results obtained by this method are somewhat low, owing to the precipitation of basic aluminium sulphate. The indications given by both helianthin and phenolphthalein in presence of salts of aluminium are less sharp than usual, and the use of litmus is quite impracticable. With ammonium alum, the end-points are still less definite, and it is necessary to expel the ammonia, by boiling with caustic alkali, before the estimation of the alumina is attempted.

The separation of aluminium from other metals may be effected by the use of baryta water, in which alumina is fairly soluble. A complete separation, however, can only be attained by repeatedly treating the precipitate with baryta water, and the test analyses given are not very satisfactory.

Estimation of Iron.—Very dilute solutions of ferrous salts may be titrated directly with caustic soda in presence of phenolphthalein; or the solution may be boiled with excess of alkali and titrated back with acid, with or without filtration. Free acid, if present, is first neutralised by addition of alkali to the end-point indicated by helianthin. The method, which consists in precipitating the oxide, dissolving it in excess of acid, and titrating back with alkali, cannot be employed, owing to the rapid oxidation of ferrous hydroxide on exposure to air. The process may, however, be successfully applied to the sulphide, obtained by precipitation with ammonium hydrosulphide.

The indications of helianthin are wholly obscured by the presence of ferric salts, and since the latter can only exist in acid solution, titration with phenolphthalein as indicator is, alone, of no value. Ferric salts must, therefore, be reduced to the ferrous state by means of hydrogen sulphide or sodium sulphite, and one of the foregoing processes then applied.

[With DELSAUX.]—*Estimation of Copper.*—The metal is precipitated as oxide, and the washed precipitate dissolved in excess of acid and titrated back with alkali, phenolphthalein being used as indicator; or both helianthin and phenolphthalein are added to the solution, the volume of standard alkali used in passing from one end-point to the other being, as usual, equivalent to the metallic oxide in solution. Satisfactory results are obtained by either method, and the colour of the solution, even when concentrated, is found to interfere in no way with the delicacy of the titration. The precipitate of cuprous oxide obtained in saccharimetry may also be estimated alkalimetrically, a considerable saving of time being thereby effected without loss of accuracy. For this purpose, the precipitate is washed with boiling water, dissolved in nitric acid, and titrated with alkali in presence of both indicators.

[With DEMOULIN.]—*Estimation of Silver.*—The method of precipitating the oxide, dissolving the precipitate in nitric acid, and titrating

back with alkali, is not to be recommended; the results obtained are too high, owing to the retention of potash by the precipitated silver oxide. Better results are got by first neutralising free acid by the addition of alkali to the end-point indicated by helianthin, adding an excess of alkali, boiling, filtering quickly, and titrating back with acid, using phenolphthalein as indicator. The end-point is not so sharp as might be wished, owing to the slight solubility of silver oxide in water.

N. L.

Separation of Aluminium. By RUDOLF L. LEFFLER (*Chem. News*, 1898, 77, 265—266).—The author finds that when a solution of aluminium chloride is boiled with sodium acetate, the aluminium is not completely precipitated, even when a large excess of acetate is used. When sufficient ammonia or sodium carbonate is added to the hot solution of chloride to cause faint opalescence, the aluminium may be completely precipitated by acetate; under these conditions, 0.25 and 0.50 gram of aluminium requires respectively 2.25 and 3.75 grams of sodium acetate for complete precipitation, and, on cooling, some aluminium is again dissolved. On account of the large excess of acetate required, aluminium cannot be separated from any other metals except manganese by this method. Nickel may be separated from aluminium by means of sodium phosphate in presence of acetic acid if an alkali is first added to the solution until it is faintly opalescent. The relative amounts of sodium phosphate and acetic acid can only be varied within narrow limits; when a solution containing 0.5 gram of aluminium and 0.1 gram of nickel per litre was treated with 30 c.c. of a saturated solution of the phosphate and 10 c.c. of acetic acid, the separation of the nickel was complete. This method does not afford a satisfactory means of separating zinc and copper from aluminium.

E. W. W.

Commercial Analysis of Bauxite. By WILLIAM B. PHILLIPS and DAVID HANCOCK (*J. Amer. Chem. Soc.*, 1898, 20, 209—225).—The authors call attention to the importance in the analysis of bauxite of discriminating between aluminium hydroxide, which, on account of its ready solubility, is so important to alum makers, and other less soluble compounds of alumina.

The following analytical method is recommended. Two grams of the sample, which should not have been subjected to any considerable heat, is heated in a dish with 10 c.c. of sulphuric acid of sp. gr. = 1.53, until sulphuric acid fumes are evolved, when a watch glass is put on, and the heating continued for 10 minutes. When cold, 100 c.c. of hot water is added, and, after boiling for five minutes, the liquid is filtered, and finally made up to 200 c.c. For the estimation of the alumina, 50 c.c. is taken, diluted to 300 c.c., 2 c.c. of hydrochloric acid added, the liquid heated to boiling, and ammonia then added in very slight excess. After boiling for 5 minutes, the precipitate is collected, washed, dried, ignited, and weighed. From its weight is subtracted the oxides of iron and titanium obtained in other operations, and it then represents the available alumina. To estimate the titanium, 50 c.c. of the solution is neutralised with ammonia until a slight precipitate occurs, which is then carefully redissolved in sulphuric acid,

after which the liquid is diluted to 400 c.c. and boiled for an hour; if iron is present, this must be reduced by continually adding sulphurous acid, and hot water should occasionally be added to replace that lost by evaporation. The titanium dioxide is completely precipitated, and can be collected, washed, dried, ignited, and weighed. The iron may be estimated in the filtrate by titration with permanganate.

In order to obtain the free alumina, 2 grams of the sample is heated with 10 c.c. of sulphuric acid of sp. gr. 1.53 at 95—100° for 1 hour in an Erlenmeyer flask having a perforated stopper, 100 c.c. of hot water is added, and after the mixture has been heated for 10 minutes, the alumina is estimated in the same way as before, but there is no necessity of looking for titanium; the small amount of ferric oxide must, however, be estimated and deducted from the weight of the alumina.

The difference between the available and the free alumina represents the combined alumina.

L. DE K.

Volumetric Estimation of Cobalt. By HARRY B. HARRIS (*J. Amer. Chem. Soc.*, 1898, 20, 173—185).—The paper is an exhaustive criticism of some of the processes in use for the volumetric estimation of cobalt.

Winkler's method, which consists in titrating the solution with standard permanganate in the presence of yellow mercuric oxide, gives fairly good results, but the author finds that it should be conducted at the boiling point of the solution. Instead of the mercury compound, a mixture of zinc oxide and ferric chloride may be used; both mercuric oxide and ferric hydroxide act mechanically on the cobaltic oxide, carrying it down, and thereby enabling the end reaction to be distinctly observed. The cobalt solution should contain about 0.1 to 0.2 gram of the metal, and comparatively small amounts of copper; ferric iron, lead, or antimony do not interfere. If arsenic is present, some ferric chloride should be added, and mercuric oxide used to carry down the cobalt. In the presence of nickel, the results are too high.

McCulloch's method, which consists in precipitating the cobalt as cobaltic cyanide, and estimating this by reducing it with ferrous sulphate, and retitrating with standard dichromate, was found to yield only 90 per cent., or even less, of the metal actually present.

Fleischer's method, which consists in oxidising an alkaline solution of cobalt and nickel with sodium hypochlorite, treating the precipitate with dilute ammonia to reduce the nickel sesquioxide, the cobaltic oxide being left unchanged, and estimating the latter by reduction with ferrous sulphate, gives utterly untrustworthy results unless the ammonia is exactly of the right strength (1 part of ammonia of sp. gr. 0.96 and 3 parts of water), and the boiling is continued for 2 hours. The amount of nickel should exceed that of the cobalt, otherwise the results may be as much as 14 per cent. too high; the best results obtained by the author still showed 2 per cent. in excess.

Donath's method consists in oxidising the cobalt with iodine in the presence of sodium hydroxide, afterwards heating the precipitate with hydrochloric acid, and estimating the liberated chlorine iodometrically; this gives fairly good results, even in the presence of nickel, but it is of prime importance that the iodine be chemically pure, otherwise part

of the nickel will also be oxidised, and the result may be nearly 30 per cent. too high.

Von Reis's method, which consists in boiling the cobalt solution with zinc oxide and adding an excess of standard permanganate, which is then titrated back with ferrous sulphate, gives results which are fairly satisfactory. The author does not state whether it is influenced by the presence of nickel. In conclusion, it is stated that a really good process is still a *desideratum*.
L. DE K.

Separations from Chromic Acid. IV. Separation of Chromium. By HARRY BREARLEY (*Chem. News*, 1898, 77, 216—218. Compare this vol., ii, 409, 460).—The author finds that chromic salts may be completely precipitated in the presence of chromates by boiling with a slight excess of sodium hydroxide, or by boiling with sodium phosphate. In the latter case, the phosphate itself may be used instead of an alkali to neutralise the free acid; the chromium phosphate when precipitated in the cold is frequently of a darker colour than that obtained from hot solutions.

When chromic salts are oxidised by means of potassium permanganate, the last portions strongly resist the action of a small excess of permanganate, and, if too much of the oxidising agent is added, some chromate may be carried down by the precipitated oxides of manganese. If too little sulphuric acid is present, the precipitated manganese oxides are partly dissolved without being completely decomposed, and too much sulphuric acid prevents complete oxidation. By adding a large excess of potassium permanganate to a solution of ferrochrome or steel, the whole of the manganous salts may be precipitated.

E. W. W.

Electrolytic Estimation of Uranium and Cadmium. By EDGAR FRANCIS SMITH and DANIEL L. WALLACE (*J. Amer. Chem. Soc.*, 1898, 20, 279—281).—Heidenreich having stated that no trustworthy results can be obtained by the authors' electrolytic process for the estimation of uranium and cadmium (*Abstr.*, 1896, ii, 545), fresh evidence is now given in support of its accuracy.

Ten c.c. of a solution of uranium acetate containing 0.1185 gram of uranouranic oxide was mixed with 0.5 c.c. of glacial acetic acid, diluted to 40 c.c., and then electrolysed for 6 hours at 70° with a current $ND_{40} = 0.18$ ampère volt. = 3. The uranium was completely deposited as hydrated protosesquioxide, which on ignition left in 3 experiments 0.1187, 0.1184, and 0.1182 gram of uranouranic oxide.

Ten c.c. of a solution of cadmium sulphate containing 0.1656 gram of metal was mixed with excess of a solution of disodium hydrogen phosphate of sp. gr. = 1.0358 and 1.5 c.c. of phosphoric acid of sp. gr. = 1.347. After diluting to 100 c.c. and heating to 50°, the liquid was electrolysed for 7 hours with a current $ND_{100} = 0.06$ ampère volt. = 3, the current at the end of 4 hours being increased to $ND_{108} = 0.36$ ampère volt. = 7. The results in three experiments were 0.1654, 0.1658, and 0.1657 gram of cadmium.
L. DE K.

Coal Analysis. By WILLIAM FRANCIS HILLEBRAND, C. B. DUDLEY, and WILLIAM ALBERT NOYES (*J. Amer. Chem. Soc.*, 1898, 20, 281—285).—This is a preliminary report from a committee appointed by the

American Chemical Society to devise uniform methods for the technical analysis of coal.

Sampling is done in the usual manner, at least five pounds of coal being employed. For the estimation of the moisture, 1 gram of the powder is heated in an open porcelain or platinum crucible for one hour at $104-107^{\circ}$, best in a double-walled bath containing pure toluene; it is then cooled in a desiccator and the crucible weighed covered. The process gives very concordant results, although higher and probably more correct results are obtained by drying in a vacuum over sulphuric acid; this, however, takes about 20 hours. In the case of bituminous coals, traces of volatile organic matters are driven off at 100° , particularly if dried in a current of air, but this does not materially affect the method.

To estimate the volatile combustible matter, 1 gram of the undried sample is placed in a platinum crucible weighing 20 to 30 grams and having a tightly fitting cover. This is then heated for 7 minutes over the full flame of a Bunsen burner. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner; the flame should be 20 to 25 cm. high when burning free, and the experiment made in a place protected from draught. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. From the loss on ignition must be deducted the loss on drying.

The amount of ash is estimated by incinerating the portion used for the estimation of the moisture, at first over a very low flame with the crucible open and inclined, until it is free from carbon. The fixed carbon is represented by the amount of coke less the ash.

No particular scheme is, as yet, proposed for the estimation of the sulphur, but as in the case of the other items, useful suggestions will be duly considered by the committee.

As the result of 21 analyses of coals, the heating effect of which had been determined with the bomb calorimeter, the following rule is proposed for calculating the heating effect from the analytical data. "Subtract from 100 the percentages of moisture and ash and one-half the percentage of sulphur, and multiply the remainder by 80.7. The product will be the heating effect of the coal burnt to vapour of water, expressed in calories."

L. DE K.

Estimation of Small Quantities of Alcohol. By FRANCIS G. BENEDICT and R. S. NORRIS (*J. Amer. Chem. Soc.*, 1898, 20, 293—302).—The reagents required for this estimation are: A solution of chromic acid prepared by dissolving 2.2064 grams of potassium dichromate in as little water as possible, and making up to 500 c.c. with concentrated sulphuric acid, taking care that the temperature shall not rise above 100° . A standard solution of alcohol made by mixing two grams of exactly 5 per cent. alcohol in a flask with 5 c.c. of sulphuric acid, avoiding rise in temperature, and then diluting with acid to 50 c.c. Solutions of ferrous ammonium sulphate and potassium permanganate standardised against each other.

Twenty c.c. of the chromic acid solution is delivered with great care from a burette into a flask containing 200 c.c. of water, and

ferrous sulphate solution is added from a burette until the chromate is entirely reduced; the unavoidable excess is titrated back with permanganate. The same amount of chromic acid solution is now mixed in a small flask with 5 c.c. of the standard alcohol and heated for 5 minutes to 98°, which temperature should on no account be exceeded; when cold, the contents are diluted with 200 c.c. of water, and the titration with iron is repeated. The difference in c.c. between the amounts of ferrous sulphate solution used to reduce the chromic acid will represent the quantity of alcohol used in the experiment.

Unknown solutions of alcohol, which are not to contain more than about 1 per cent., are first tested by specific gravity, which will give a rough indication of the percentage of alcohol. Enough of the sample is then weighed out to approximately correspond with the amount of real alcohol used in the check experiment; this is mixed with twice its bulk of sulphuric acid, 20 c.c. of the chromic acid solution is added, the whole heated to 98° as before, and after diluting with 200 c.c. of water, titrated with ferrous sulphate.

L. DE K.

Estimation of Methoxy-groups. By GEORG GREGOR (*Monatsh.*, 1898, 19, 116—121).—Two slight modifications in Zeisel's method are suggested. (1) The alcoholic silver nitrate solution should be strongly acidified with nitric acid, when the alkylic iodide is more readily decomposed, and the precipitate at most contains traces of silver nitrate, easily removable by water, whereas when a neutral silver solution is employed, it is always hard to remove the silver nitrate mechanically carried down by the haloid salt. (2) There is always some slight reduction of the silver nitrate solution, caused, as the author has definitely proved, by traces of the amorphous phosphorus, used to retain the evolved hydriodic acid, being carried over. This error is easily overcome by the use of a solution of arsenious acid in potassium carbonate, the former arresting any free iodine, and the latter the hydriodic acid.

A. W. C.

Solubility of Pentosans in the Reagents Employed in the Estimation of Starch. By WILLIAM H. KRUG and HARVEY WASHINGTON WILEY (*J. Amer. Chem. Soc.*, 1898, 20, 266—268).—In one of the processes for the estimation of starch, the material is heated under pressure with a dilute solution of lactic or salicylic acid; the authors find, however, that these liquids act on the pentosans so much, that the latter may lose from 80 to 90 per cent. of their weight, and thus cause an apparent increase in the percentage of the starch.

Contrary to König's statement, who asserts that pentosans are dissolved when using the diastase process, the authors find that pentosans are scarcely affected, so that the diastase process is the only trustworthy method for estimating starch.

L. DE K.

Comparison of the Standard Methods for the Estimation of Starch. By HARVEY WASHINGTON WILEY and WILLIAM H. KRUG (*J. Amer. Chem. Soc.*, 1898, 20, 253—266).—The authors reject as untrustworthy the processes based on polarisation, at present in use. The method devised by Lindet, which is founded on the direct weighing of

the starch after treatment with pepsin to dissolve the proteid envelope of the starch cells, is far too tedious and not very accurate, some starch remaining with the fibre, whilst, on the other hand, some fibre gets into the starch. Good results may, perhaps, be obtained by combining this method with the diastase process, but this subject is still being investigated.

The best results are obtained by the diastase process without pressure. The finely-ground sample should be thoroughly extracted with ether to remove fat, and then be treated twice with freshly prepared diastase at 50°. To make sure that all the starch has been removed, the residue should be examined microscopically for starch granules. The authors think taka-diastase may be successfully employed; it acts more slowly than ordinary diastase, but may be readily obtained free from sugars.

L. DE K.

Hübl's Iodine Addition Process. By J. J. A. WIJS (*Zeit. anal. Chem.*, 1898, **37**, 277—283).—Schweitzer and Lungwitz (*Abstr.*, 1895, ii, 398) called attention to the development of acid during the action of Hübl's reagent on a fat, which acid they assumed to be hydriodic acid. The author quotes an experiment with an unnamed oil, in which, although a considerable development of acid took place, this did not liberate iodine from potassium iodate until an iodide was added, and could, therefore, not be hydriodic. He admits that the proof is imperfect, as water was added before titrating, and this produced a precipitate of mercuric iodide which may have resulted, in part, from double decomposition between hydriodic acid and mercuric chloride. He, nevertheless, advances another hypothesis, namely, that direct combination occurs between the fat and iodine chloride, which is almost certainly present in Hübl's reagent, and that the compound formed then undergoes dissociation, with separation of hydrochloric acid, and, in proof that this development of acid is the result of a mass action, he adduces experiments showing that the more free acid is present in the Hübl reagent, the less acid is developed during the iodation of a fat, although the amount of halogen absorbed is but slightly influenced thereby. Further, when equal quantities of the same specimen of reagent are caused to act on varying amounts of fat, the amount of acid developed is proportional to the amount of halogen absorbed, even when the quantity of fat is too large to be fully iodated. Fats having such widely different iodine numbers as linseed oil and coconut oil, show the same proportion of acid developed to total halogen absorbed, whilst substances of different constitution, such as amylic alcohol and cholesterol, show widely different proportions. Lastly, the greater the solubility of hydrochloric acid in the fat solvent, the larger is the proportion of acid developed, which fact is most in accord with the dissociation hypothesis.

M. J. S.

Rancidity of Fats. By A. SCHMID (*Zeit. anal. Chem.*, 1898, **37**, 301—303).—The acidity of a fat is not, as was formerly assumed, a measure of its rancidity; a fat is acid when it contains an abnormally high proportion of free fatty acids; it is rancid when the glycerol has undergone partial or complete oxidation to aldehydes and ketones. The latter may be detected by distilling the fat with steam and collecting

the distillate in a flask containing a freshly prepared 1 per cent. solution of metaphenylenediamine hydrochloride, with which reagent the distillate from a rancid fat gives a yellow or yellowish-brown coloration, whilst a fresh fat gives the merest trace of yellow. Collaboration of other chemists is invited for the confirmation of this criterion of rancidity, and also for the fixation of limits. M. J. S.

Testing of Indigo. By ALBERT BRYLINSKI (*Chem. Centr.*, 1897, ii, 913—914; from *Bull. Soc. ind. Mulhouse*, 67, 331—345).—The indigo is first sulphonated by heating 1 gram of the sample with 20 grams of powdered glass and 25 c.c. of sulphuric acid of sp. gr. = 1.85 for 6 hours at 100°; this temperature must be kept constant, otherwise compounds of a violet colour will be formed, which are not suitable for colorimetric estimation or titration. All processes based upon oxidation should be rejected, as the other constituents of the indigo are then estimated as indigo. Of methods involving reduction there are two in use, namely, the hyposulphite method and Engel's vanadium sulphate process; of these, the author prefers the latter, which is best conducted as follows: 10 grams of ammonium vanadate is dissolved in 100 grams of concentrated sulphuric acid with the aid of a gentle heat and poured into 2 litres of water at 50°. Fifty grams of zinc dust is then added, and the whole shaken until a pure, bluish-violet liquid is obtained. The analysis and the measuring off of the vanadium solution should be conducted out of contact with the air, best in an atmosphere of carbonic anhydride.

The vanadium solution is checked with a known weight of pure indigo, and is run in until the indigo solution becomes yellow, the final end-reaction being shown by a dirty-green colour. If ferric salts are present a little vanadium trioxide dissolved in sulphuric acid should be added to the indigo to reduce the iron to the ferrous state.

L. DE K.

Testing Diastatic Substances. By JOKICHI TAKAMINE (*Chem. News*, 1898, 77, 173).—Eight glasses of 150 c.c. capacity are placed side by side in a pan of water at about 40°, into each is put 100 c.c. of starch solution, and into the first 1 c.c. of the saliva or other liquid to be tested, whilst the other seven glasses receive from 1 c.c. up to 7 c.c. of standard diastase solution; the contents are stirred, and when the liquefaction of the paste is complete, a drop from each of the seven glasses is spread on a glazed plate and treated with a drop of iodine solution giving a scale of colour with which the contents of the first tube is compared; these tests are repeated within the first 10 minutes after the addition of the saliva. The starch solution is prepared by stirring 50 grams of neutral potato starch with 200 c.c. of cold water, adding 800 c.c. of boiling water, and boiling the mixture for two minutes. For the iodine solution, 1 gram of iodine and 2 grams of potassium iodide are agitated with about 5 c.c. of water until dissolved and then diluted to 120 c.c. The standard diastase solution is made fresh each day by dissolving, in 100 c.c. of water, 1 gram of taka-diastase solution that has been standardised by Lintner's or Junk's method.

D. A. L.

General and Physical Chemistry.

Phosphorescent Strontium Sulphide. By JOSÉ R. MOURELO (*Compt. rend.*, 1898, 126, 904—906).—When phosphorescent strontium sulphide is very intimately mixed with not more than 19 times its own weight of calcium, strontium, or barium sulphate, the whole mass becomes uniformly phosphorescent when excited. Sometimes it is necessary to reheat the mixture in order to secure this result. The intensity of the phosphorescence and the excitability are lower than with the pure sulphide, and the colour of the phosphorescence is somewhat paler. The results depend on the volume of the mass; and other things being equal, the phosphorescence is most intense with barium sulphate, and least with calcium sulphate. C. H. B.

Spectra of Iodine. By HEINRICH KONEN (*Ann. Phys. Chem.*, 1898, [ii], 65, 257—286).—A measurement of the lines in the emission and absorption spectra of iodine from $\lambda = 3030\cdot5$ to $\lambda = 6191$ in Ångström units. In vacuum tubes, either a line or a band spectrum can be obtained. The band spectrum is made up of two different parts, B_R and B_V ; of these, B_R is identical with the absorption band spectrum, but B_V is not. If the discharge is sufficiently powerful, B_R disappears, whilst B_V gains in intensity, and the author is therefore inclined to assign B_R to the ordinary molecules of iodine and the occurrence of B_V to dissociation. Two series may also be distinguished in the line spectrum, but it is possible that the second series in this case is due to the presence of some impurity. The measurements are given in tabular form. H. C.

Zeeman's Phenomenon: Variations of Spectra in Magnetic Fields. By HENRI BECQUEREL and HENRI DESLANDRES (*Compt. rend.*, 1898, 126, 997—1001).—The authors have extended the observations of Lorentz and Zeeman, Cornu and Michelson on the variations observed in spectra when the luminous bodies are within a strong magnetic field. They find that, under the influence of the field, a line may be split up in such a way that components polarised in a plane perpendicularly to the field enclose the components polarised in a plane parallel with the field, this being a mode of division which was not described by Michelson, and which is contrary to that usually observed. Special attention was given to the spectrum of iron, and the following table shows the influence of the magnetic field on a portion of the spectrum between $\lambda 387$ and $\lambda 382$.

Normal wave-lengths.	Differences of wave-length in the magnetic field ; lines polarised in a plane	
	Normal to the field.	Parallel with the field.
3872·61	0·207	0·383
3865·65	0·368	0
3860·03	0	0·369
3858·40 (Ni)	0	0·293

Normal wave-lengths.	Differences of wave-length in the magnetic field ; lines polarised in a plane	
	Normal to the field.	Parallel with the field.
3856·49	0	0·355
3850·10	0	0
3841·19	0	0·184
3840·58	0	0·159
3834·37	0	0·230
3824·58	0	0·360
3820·64	0	0·287

It is noteworthy that the line 3850·10 does not become multiplied, although the neighbouring lines show the phenomenon. The line 3865·65 is resolved into a triplet, but, unlike other lines, it shows a distinct subdivision in the spectrum polarised in a plane normal to the field, and a slight thickening in the spectrum polarised in a plane parallel with the field.

These peculiarities show that a magnetic field may render evident differences as yet unobserved between the lines of one and the same element or between lines of the same spectrum, and the authors suggest that some of the spectral lines not hitherto recognised as belonging to any particular substance may really be due to the effects of magnetic influence.

The carbon band at $\lambda 388$ found in the spectra of the sun and of comets, and remarkable for the number and regular order of its component lines, shows no recognisable splitting up or enlargement of the lines in a magnetic field, although the calcium lines, under the same conditions, show the usual subdivision. Zeeman found no alteration in the bands of iodine.

All the observations hitherto made seem to show that the influence of the magnetic field is greatest in the case of lines of high wave-length.
C. H. B.

Connection between Volume Change and Specific Rotation of Active Solutions. By RICHARD PRIBRAM and CARL GLÜCKSMANN (*Monatsh.*, 1898, 19, 122—137, 161—170, and 171—177. Compare this vol., ii, 321).—Aqueous solutions of tartaric acid show a maximum contraction in volume at a point corresponding with about 16 per cent. of the dissolved acid; in concentrated solutions, a dilatation occurs. The specific rotation also changes with concentration in an irregular manner, several changes in the direction of the specific rotation curve occurring, and distinct breaks in continuity being observed at the concentrations 1·116, 4·669, about 16, and about 36 per cent.

In solutions of potassium tartrate, no point of maximum contraction is reached, but the contraction increases regularly with the concentration. There are three breaks on the specific rotation curve, these corresponding with the concentrations 9·03, about 17·2, and 30·84 per cent. The behaviour of sodium tartrate resembles that of the potassium salt, two breaks occurring in the specific rotation curve at 6·755 and 19·09 per cent.
H. C.

Optical Activity. By L. TCHUGAEFF (*Ber.*, 1898, 31, 1775—1782. Compare this vol., ii, 274).—The following numbers have been obtained for the ethereal salts of *l*-borneol with normal acids.

	$[\alpha]_D$	$[M]_D$	$d\ 20^\circ/4^\circ$	B. p. at 15 mm.
<i>l</i> -Borneol	-39.0°	-60.0		
Bornylic formate	-40.46	-73.6	1.0058	97°
„ acetate	-44.40	-87.0	0.9855	107
„ propionate	-42.06	-88.2	0.9717	118
„ butyrate.....	-39.15	-87.8	0.9611	128
„ valerate	-37.08	-88.2	0.9533	139
„ octoate	-31.45	-88.1	0.9343	175

Thus the function $[\alpha]_D$ reaches a maximum with the acetate, and then gradually diminishes, whilst the molecular rotation $[M]_D$ remains practically constant after this salt is reached.

The influence of the phenylic group on the rotation of menthol is illustrated by the following table.

	$[\alpha]_D$	$[M]_D$	$d\ 20^\circ/4^\circ$	B. p. at 15 mm.
Menthol	-50.0°	-78.0		
Menthyllic benzoate	-90.9	-236.3		180°
„ phenylacetate	-69.57	-190.7	0.9874	197
„ phenylpropionate	-56.21	-161.9	0.9851	203
„ orthotoluato	-84.42	-231.3	0.9972	191
„ metatoluato	-87.94	-241.0	0.9931	197
„ paratoluato	-92.15	-252.5		200

The author compares these results with those obtained by Guye and Chavanne for the aromatic salts of *l*-amylic alcohol, and by Frankland and MacGregor for derivatives of active glyceric acid; he points out that they illustrate the moderating effect which distance from the active complex exerts on the increase of rotation produced by the phenylic group. The same influence will be recognised in the optical difference between the ethereal salts $C_5H_{11}\cdot S\cdot CS\cdot OEt$ and $C_5H_{11}\cdot O\cdot CS\cdot S\cdot Et$; the former has the specific rotatory power $[\alpha]_D = 15.02^\circ$, the molecular rotation $[M]_D = 28.8^\circ$, and a sp. gr. = 1.0184 at $20^\circ/4^\circ$, whilst the corresponding constants for the latter salt are 6.32° , 12.1° , and 1.0167 respectively.

Amylic sulphite, $SO(O\cdot C_5H_{11})_2$, which boils at 127° under a pressure of 15 mm., has a sp. gr. 0.9841 at $20^\circ/4^\circ$, the specific rotatory power $[\alpha]_D = 4.03^\circ$, and the molecular rotation $[M]_D = 8.95^\circ$. It conforms, therefore, to the law of superposition enunciated by Guye and Gautier (*Abstr.*, 1895, ii, 149).

M. O. F.

Weston Standard Cell. By PH. KOHNSTAMM and ERNST COHEN (*Ann. Phys. Chem.*, 1898, [ii], 65, 344—357).—The Weston standard

cell, in which cadmium replaces the zinc used in cells of the Clark type, has been examined by Jaeger and Wachsmuth (*Abstr.*, 1897, ii, 86). These authors found irregularities in the behaviour of certain of the cells dealt with between 0° and 15° , and the present investigation was undertaken for the purpose of ascertaining the cause of this peculiarity. Attention was in the first place directed to the crystallised cadmium sulphate used in the cell. As some doubt exists with reference to the composition of this salt, careful analyses were made and were found to be in agreement with the usually accepted formula, $3\text{CdSO}_4 + 8\text{H}_2\text{O}$. Solubility determinations and the investigation of some other properties of the solutions show that this salt undergoes some change at 15° , and that it is this change which affects the behaviour of the Weston cell at this temperature. The salt does not, however, appear to change in composition. For practical purposes, therefore, the use of the Weston cell should be restricted to temperatures above 15° .
H. C.

A New Accumulator. By DONATO TOMMASI (*Bull. Soc. Chim.*, 1897, [iii], 17, 211—213).—The electrodes consist of a perforated tubular envelope or case of celluloid enclosing a central grid of lead-antimony alloy, the intervening space being filled with a paste of lead oxide and dilute sulphuric acid. The normal discharge varies from 1 to 4 ampères per kilogram of electrode, but may, on occasion, be increased to 12 or 15 ampères without inconvenience. The initial E.M.F. is 2.4 volts; mean E.M.F., 2 volts; capacity per kilogram of electrodes, 22—25 ampère-hours; efficiency in ampère-hours, 95 per cent.; efficiency in watt-hours, 80 per cent.
N. L.

Electrical Conductivity of Dilute Solutions of Potassium Permanganate. By EMMANUEL LEGRAND (*Compt. rend.*, 1898, 126, 1025—1027).—The molecular conductivity of potassium permanganate in aqueous solution increases with the dilution, and at 25° tends towards a limit, 124, which coincides with that obtained by other observers for normal salts at the same temperature. The resistance diminishes as the temperature rises, the rate of diminution being smaller the higher the temperature. The temperature coefficient varies but little with the dilution.
C. H. B.

Galvanic Polarisation. By HANS JAHN (*Zeit. physikal. Chem.*, 1898, 26, 385—429).—The author has repeated and extended his previous investigations on the polarisation of a cell and the energy requisite for the decomposition of the electrolyte (*Abstr.*, 1896, ii, 230); the present values are regarded as more accurate than those previously given; this is due, chiefly, to the use of a large ice calorimeter, which renders possible more accurate measurements of the thermal changes. The values obtained are given in the accompanying table, where p_0 , p_{40} are the polarisations in volts at 0° and 40° ; dp/dt is the temperature coefficient of the polarisation; ω , the energy in calories necessary for the decomposition of a milligram-equivalent of the electrolyte at 20° ; ω_k and ω_a , the heat developments at the cathode and anode respectively, calculated as indicated in the previous paper.

Salt.	n_0	p_{40}	$\frac{dp}{dt}$	ω	ω_k	ω_a
CuSO ₄	1.57	1.43	-0.0038	67.77	-10.07	+21.84
ZnSO ₄	2.62	2.48	-0.0035	115.98	-10.17	+20.06
CdSO ₄	2.33	2.18	-0.0038	102.34	-8.77	+21.13
Cu(NO ₃) ₂	1.56	1.42	-0.0035	67.77	-10.07	+25.43
Pb(NO ₃) ₂	2.03	1.89	-0.0035	89.15	-2.43	+23.51
Ag ₂ (NO ₃) ₂	1.10	0.99	-0.0028	47.30	+2.53	+28.17

It is seen that, except in the case of silver nitrate, the temperature coefficient and anodic heat are practically identical for all the salts. If the values for the cathodic polarisation be subtracted from the above polarisation values, the resulting anodic polarisations are found to be identical, within experimental error, for all the salts examined, a result which is also theoretically deduced for the salts of all strong acids; for weak acids, however, smaller values should obtain. The investigations were extended to oxy-acids, and by the thermodynamical equations deduced by the author and Schönrock (Abstr., 1895, ii, 178), the value of the polarisation E.M.F is calculated for sulphuric acid, and from this the loss of heat of the battery; the values obtained agree completely with the direct determinations. If, in the electrolysis of normal sulphuric acid, an anode of electrolytically deposited copper be employed, the total loss of heat should be equal to the difference between that due to the acid and that due to the copper sulphate, and this also was experimentally verified. According to the previous theoretical investigations, the polarisation is independent of the dissociation if the current is weak, and it was found to be so for the polarisation in phosphoric acid. The polarisation, however, being dependent on the occlusion of gas by the electrode, should vary with different electrodes, and the author found that, by the use of a mercury cathode, the polarisation in sulphuric acid reached 2.95 volts, the loss of heat being 50 per cent. greater than with the platinum cathode. In the case of the alkali salts, the polarisation should be equal for those salts the hydroxides of which are equally dissociated, and this was verified by determinations of the polarisation in solutions of sodium and lithium sulphates; ammonium sulphate, however, owing to the more feeble dissociation of the hydroxide, gave a much smaller value.

L. M. J.

Dissolving of Platinum and Gold in Electrolytes. By MAX MARGUELES (*Ann. Phys. Chem.*, 1898, [ii], 65, 629—634).—An electromagnet with armature serves as contact breaker to the current from two Daniell cells, and between the terminals of the coil of the magnet an electrolytic cell with gold or platinum electrodes is introduced. With this arrangement, the metal can be dissolved in hydrochloric, nitric, or sulphuric acid, or in potassium or sodium hydroxide. The metals always dissolve from the electrode, which is the anode to the battery current. The solution is, however, in some way assisted by

the current from the magnet, as neither a constant nor intermittent current from the battery alone is capable of effecting solution.

H. C.

Heat of Dissolution and of Dilution. By ED. VON STACKELBERG (*Zeit. physikal. Chem.*, 1898, **26**, 533—563).—The author determined the heats of dissolution and of dilution, at various concentrations, for the following compounds—potassium nitrate, chlorate, bromate, iodate, perchlorate, dichromate, and chloride, barium nitrate, ammonium chloride, sodium chloride, sodium nitrate, and cane-sugar. In most cases, the determinations were made at from 16—18°, but a few values at 0° were also obtained. With the exception of that for cane-sugar, the curves of heat of solution against concentration are all very similar, being convex to, and approaching, the axis of concentration. Between the values for N/200 and N/∞ solutions, a difference of from 5 to 15 per cent. usually occurs, except in the case of ammonium chloride, where dilution beyond N/200 has but little effect. The heat of dilution is greater at low than at high temperatures, and in sufficiently dilute solutions the same obtains for the heat of solution. The heat of dilution may be regarded as due to two causes, (1) changes in the dissociation of the dissolved compound, (2) changes in the internal pressure of the solution. The heat effects, due to the latter cause, are calculated from Tammann's results (*Abstr.*, 1896, ii, 513) and added to those due to the dissociation, but the sum does not agree with the heat of dilution found experimentally. The temperature coefficient of both heat of dissolution and of dilution is theoretically investigated, and the results obtained are verified by the experimental values. The temperature coefficient may be also calculated from the solubility at different temperatures, and in the case of potassium chlorate the results obtained are shown to be in accord with the determinations. The case of changes in hydration of a salt is also discussed, and the author points out that the heat of hydration for $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} + 3\text{H}_2\text{O}$ must change in sign with increase of temperature, inasmuch as the solubility curve of this compound, if sufficiently produced, cuts that of the higher hydrate in two points.

L. M. J.

Heat of Neutralisation of Ethylphosphoric Acid. By G. BELUGOU (*Compt. rend.*, 1898, **126**, 1151—1152).—The heat of neutralisation of ethylphosphoric acid in dilute aqueous solution by dilute potassium hydroxide solution is, for successive equivalents +15.5 Cal., +13.8 Cal., +2.8 Cal. The corresponding values for glycerophosphoric acid are +15.4 Cal., +13.9 Cal., and +0.4 Cal., and for phosphoric acid +15.9 Cal., +11.1 Cal., and +6.6 Cal.

It follows that, in ethylphosphoric acid, it is the alcoholic function that has disappeared, whilst the strong and weak acid functions remain and correspond with those of glycerophosphoric acid. The heat of neutralisation of the weaker acid function is higher than the corresponding value for phosphoric acid.

The heat developed by the action of the third equivalent of alkali probably indicates that dipotassium ethylphosphate is partially hydro-

lysed in presence of excess of potassium hydroxide (compare Abstr., 1894, ii, 484, and following abstract). C. H. B.

Alkyl-Phosphoric Acids. By JACQUES CAVALIER (*Compt. rend.*, 1898, 126, 1142—1144; see also Abstr., 1894, ii, 484).—The alkyl-phosphoric acids, PO_4RH_2 , in which R is Et, Me, or C_3H_5 are dibasic acids, which yield normal salts, $\text{PO}_4\text{RM}'_2$, and acid salts, PO_4RHM . They are acid to methyl-orange and phenolphthalein, but the mono-metallic salts are neutral to methyl-orange, and the normal salts are neutral to phenolphthalein. With the latter indicator, the end-point is more distinct than with phosphoric acid. The heats of neutralisation are as follows.

		PO_4MeH_2 .	PO_4EtH_2 .	$\text{PO}_4(\text{C}_3\text{H}_5)_2\text{H}$.
1st equivalent.....	NaOH	15.49 Cal.	15.59 Cal.	15.56 Cal.
2nd " 	NaOH	14.11 "	13.80 "	14.00 "
1st " 	KOH	15.85 "	15.73 "	— "
2nd " 	KOH	14.05 "	13.61 "	— "
1st " 	NH_3	14.36 "	14.44 "	14.24 "
2nd " 	NH_3	12.36 "	12.03 "	12.57 "
1st " 	$\text{Ba}(\text{OH})_2$	15.80 "	16.30 "	15.90 "
2nd " 	$\text{Ba}(\text{OH})_2$	14.10 "	13.88 "	14.00 "

The heats of neutralisation of the three acids are practically identical. The first equivalent of alkali develops more heat than the second, and in both cases the development of heat is greater than with phosphoric acid. It follows that when an atom of hydrogen in phosphoric acid is displaced by a saturated or unsaturated alkyl radicle, it is the feeble acidic function that disappears, and there remain two acidic functions, the values of which are unequal, but are independent of the nature of the alkyl group substituted for the hydrogen. From the description of glycerophosphoric acid given by Imbert, Astruc, and Belugou, it would seem that these conclusions hold good even when the radicle substituted for hydrogen is a complex radicle containing hydroxyl groups. C. H. B.

Dialkyl Hydrogen Phosphates. By JACQUES CAVALIER (*Compt. rend.*, 1898, 126, 1214—1215).—The dialkyl hydrogen phosphates, $\text{PO}_4\text{R}_2\text{H}$, when R is methyl, ethyl, or allyl, behave like strong acids, and may be accurately titrated with alkalis, either methyl-orange or phenolphthalein being used as indicator. The following heats of neutralisation were determined.

	$\text{PO}_4\text{Me}_2\text{H}$.	$\text{PO}_4\text{Et}_2\text{H}$.	$\text{PO}_4(\text{C}_3\text{H}_5)_2\text{H}$.
NaOH	15.58 Cal.	16.35 Cal.	15.12 Cal.
KOH	— "	16.57 "	— "
$\frac{1}{2}\text{Ba}(\text{OH})_2$	15.91 "	16.76 "	15.58 "

These numbers approach those corresponding with the addition of the first molecule of base to the monalkyl dihydrogen phosphates, and are decidedly greater than those corresponding with the addition of the second molecule. In the transition from phosphoric acid to the derivatives PO_4RH_2 and $\text{PO}_4\text{R}_2\text{H}$, the feeblest acid function is the first to disappear. N. L.

Heat of Formation of Quinones of High Molecular Weight. By AMAND VALEUR (*Compt. rend.*, 1898, 126, 1148—1151).—The author's results in calories are summarised in the following table.

	M. p.	Heat of combustion.		Heat of formation.
		Const. vol.	Const. press.	
α -Naphthaquinone...	125°	1103·4	1103·7	+46·8
β -Naphthaquinone...	114—120	1110·0	1111·3	+39·7
α -Naphthol.....	95	1187·6	1188·5	+30·5
β -Naphthol.....	122	1189·4	1190·3	+28·7
Anthraquinone	281	1547·9	1548·5	+47·7
Phenanthraquinone	196	1547·4	1548·0	+48·2
Retenequinone	197	2156·4	2158·0	+91·4

There is a notable difference between α -naphthaquinone and β -naphthaquinone, which corresponds with the known differences between their properties, but the values for α -naphthol and β -naphthol are practically identical. The formation of naphthols from naphthalene develops more heat than the formation of phenol from benzene, and the conversion of α -naphthol into the quinone develops more heat than the corresponding change in the case of phenols containing more than six carbon atoms.

The heats of formation of the quinones throw no light on the question of their diketonic constitution. The diketones are formed from saturated hydrocarbons by elimination of $2\text{H}_2\text{O}$ and combination with O_2 , but the quinones are formed from closed chain hydrocarbons by combination with O_2 , and elimination of H_2O only. In this respect, it is the acids in the aliphatic series that are the analogues of the quinones, but the heat of formation of the acids from the corresponding hydrocarbons is practically independent of the molecular weight, whereas, in the case of the quinones, the heat of formation from the hydrocarbons increases distinctly with the molecular weight.

C. H. B.

Thermochemistry of Quinoneoximes. By AMAND VALEUR (*Compt. rend.*, 1898, 126, 1205—1208).—

	Heat of Combustion.		Molecular heat of formation.
	1. At constant volume.	2. At constant pressure.	
Benzoquinoneoxime (nitrosophenol).....	715·5 Cal.	715·4 Cal.	+22·9 Cal.
Thymoquinoneoxime	1334·3 „	1335·3 „	+56·2 „
α -Naphthaquinoneoxime (α -nitroso- α -naphthol) ...	1166·4 „	1166·5 „	+18·0 „
β -Naphthaquinone- β -oxime (β -nitroso- α -naphthol)...	1170·0 „	1170·4 „	+14·4 „
β -Naphthaquinone- α -oxime (α -nitroso- β -naphthol) ...	1169·6 „	1169·7 „	+14·8 „

The differences between the heats of combustion of the quinones and of their oximes are as follows.

Benzoquinone.....	656·8	Oxime	715·4	Diff.	58·6 Cal.
Thymoquinone ...	1274·6	Oxime	1335·3	,,	60·7 ,
α -Naphthaquinone	1103·7	Oxime	1166·5	,,	62·8 ,
β -Naphthaquinone	1110·3	α -Oxime	1169·7	,,	59·4 ,
β -Naphthaquinone	1110·3	β -Oxime	1170·4	,,	60·1 ,

These numbers indicate that the replacement of an atom of oxygen by the oxime group ($\text{:N}\cdot\text{OH}$) raises the heat of combustion by about 60 Cal.

J. J. S.

Combination of Pyridine and Trimethylamine with Formic and Acetic Acids. By GUSTAVE ANDRÉ (*Compt. rend.*, 1898, 126, 1105—1107).—The author has previously described the compounds of pyridine with formic and acetic acids respectively $2\text{C}_5\text{NH}_5, 5\text{H}\cdot\text{COOH}$ and $2\text{C}_5\text{NH}_5, 5\text{CH}_3\cdot\text{COOH}$.

The heat of the dissolution of the formic acid compound is $-0\cdot9$ Cal., and the heat of neutralisation of $5\text{H}\cdot\text{COOH}$ by $2\text{C}_5\text{NH}_5$ in presence of water, is $+8\cdot3$ Cal., and therefore the combination of $5\text{H}\cdot\text{COOH}$ with $2\text{C}_5\text{NH}_5$ develops $+15\cdot25$ Cal. Direct determination gave $+15\cdot3$ Cal. Similarly, for the acetic acid compound, the heat of dissolution is $+7\cdot85$ Cal., the heat of neutralisation $+7$ Cal., and the heat of combination between liquid acid and liquid base $+5\cdot75$ Cal. Direct determination gave $+5\cdot9$ Cal.

Formic acid and trimethylamine readily combine to form a compound, $5\text{H}\cdot\text{COOH}, 2\text{NMe}_3$, which boils, apparently without decomposing, at $178\cdot5$ — 180° under a pressure of $749\cdot5$ mm., and at $95\cdot5$ under a pressure of 16 mm. The vapour density shows, however, that the compound is completely dissociated. Acetic acid forms a similar compound not strictly analogous in composition, $4\text{MeCOOH}, \text{NMe}_3$, which boils at 150 — 154° under a pressure of $755\cdot5$ mm., and at 80 — 81° under a pressure of 37 mm., and is completely dissociated when in the form of vapour. The trimethylamine compounds seem to be somewhat more stable than the pyridine compounds, and it is noteworthy that their boiling points are distinctly higher than those of either of their respective constituents.

C. H. B.

Thermochemistry of Quinoline Bases. By MARCEL DELÉPINE (*Compt. rend.*, 1898, 126, 964—967, and 1033—1036).—

Base.	Molecular heat of combustion.		Molecular heat of formation.
	1. At constant volume.	2. At constant pressure.	
Quinoline	1122·3 Cal.	1123·0 Cal.	$-32\cdot8$ Cal.
Tetrahydroquinoline	1226·56 ,	1227·8 ,	$+0\cdot4$,
α -Methylquinoline	1286·27 ,	1287·25 ,	$-33\cdot75$,
α -Methyltetrahydroquinoline	1380·56 ,	1382·1 ,	$+9\cdot1$,
Isoquinoline	1123·0 ,	1123·7 ,	$-33\cdot5$ (solid)
Hydroisoquinoline	1213·75 ,	1215·0 ,	$+13\cdot2$ (liquid)

The following are the data for the hydrochlorides, the corresponding numbers are also given for aniline in order to compare with those of

the quinoline bases; and the numbers for benzylamine and methylaniline are given for comparison with those of the isoquinoline bases.

Base	Heat of saturation.				Heat of solution of the hydrochloride (1 mol. = 4 litres).
	Bases.			All dissolved.	
	HCl dissolved.	Salt dissolved.	HCl gas.		
	HCl = 4 litres.	2HCl = 6 litres.			
Quinoline, anhydrous ...	6·46 Cal.	6·58 Cal.	26·80 Cal.	5·46 Cal.	-2·95 Cal.
„ (+1·5H ₂ O) ...	5·23 „	—	—	—	—
Hydroquinoline	7·15 „	7·25 „	28·05 „	—	-3·50 „
α-Methylquinoline	8·80 „	8·85 „	28·10 „	—	-1·90 „
α-Methylhydroquinoline	8·45 „	8·50 „	27·85 „	—	-2·0 „
Aniline	7·44 „	8·34 „	27·57 „	7·44 „	-2·73 „
Isoquinoline (liquid) ...	6·35 „	6·4 „	27·0 „	—	-3·25 „
„ (solid)	5·01 „	—	25·66 „	—	—
„ (hydrate)	5·41 „	—	—	—	—
Hydroisoquinoline (liq.)	12·93 „	—	34·29 „	9·92 „	-3·96 „
Benzylamine (liq.)	15·46 „	—	36·69 „	12·90 „	-3·83 „
Methylaniline (liq.).....	6·9 „	8·2 „	24·3 + D	—	-D

Quinoline bases.—

C₉H₇N liq. + water = C₉H₇N diss. + 1 Cal.

C₉H₇N liq. + 1·5H₂O = C₉H₇N, 1·5H₂O liq. + 1·23 Cal.

C₉H₇N, 1·5H₂O + water = C₉H₇N diss. + 0·23 Cal.

C₉H₇N liq. + 2H₂ gas = C₉H₁₁N liq. + 2 × 16·6 Cal.

C₁₀H₉N liq. + 2H₂ gas = C₁₀H₁₃N liq. + 2 × 21·5 Cal.

Isoquinoline.—C₉H₇N liq. + 2H₂ gas = C₉H₁₁N liq. + 2 × 23·5 Cal.

J. J. S.

Atomic Weights by Physical and Chemical Methods. By DANIEL BERTHELOT (*Compt. rend.*, 1898, 126, 1030—1033).—The atomic weights of hydrogen, nitrogen, oxygen, and carbon deduced from molecular volumes and relative densities (next abstract) are almost identical with the best determinations by chemical methods.

	O.	H.	N.	C.
Physical method	16	1·0074	14·007	12·007
Chemical method.....	16	1·0023—1·0075	14·012	12·001—12·005

It follows that the atomic weights deduced simply from determinations of relative density and compressibility confirm the results obtained by chemical methods, and in some cases are the more accurate of the two.

C. H. B.

Molecular Weights of Gases. By DANIEL BERTHELOT (*Compt. rend.*, 1898, 126, 954—956).—In consequence of the differences between the coefficients of expansion and compressibility, the molecular weights of gases are proportional, not to the actual density, but to the product of this value into the molecular volume. The molecular

volume of a gas is given by the formula $v_0 = v \frac{p}{p_0} [1 + a(p - p_0)] = v \frac{p}{p_0} (1 + ap - ap_0)$, where v is the actual volume under an infinitely small pressure p , whilst p_0 is the normal pressure and a is a coefficient

which, according to Regnault, is constant between 1 atmos. and 6 atmos., and which, in the light of Amagat's experiments, may be assumed to hold good between 1 atmos. and 0 atmos. If p is infinitely small, and p_0 is one atmosphere, the relation between the molecular volumes of two gases is given by the expression $v_0/v'_0 = (1 - a) \div (1 - a')$. If d and d' are their respective densities, their molecular weights are proportional to $(1 - a)d$ and $(1 - a')d'$.

The following table gives (1) the value of a at 0° ; (2) the molecular volume v_m at 0° and atmospheric pressure; (3) the sp. gr. d with reference to oxygen as a standard; (4) the molecular weight M when $0 = 32$, and (5) the atomic weight μ when $0 = 16$.

	H.	N.	CO.	O.
a	-0.00046	+0.00038	+0.00046	+0.00076
v_m	1.00046	0.99962	0.99954	0.99924
d	0.062865	0.87508	0.87495	1
M	2.01472	28.0132	28.0068	32
μ	1.0074	14.007	12.007	16

C. H. B.

Determination of the Molecular Weight of Solid Substances. By ANDREAS FOCK (*Ber.*, 1898, 31, 1610—1611).—A reply to I. Traube (this vol., ii, 369).

M. O. F.

Molecular Association of Liquids. By WILHELM VAUBEL (*J. pr. Chem.*, 1898, [ii], 57, 337—356).—The molecular association of liquids can be easily determined by dividing the actual heat of vaporisation by the heat of decomposition, the latter standing in direct relation to the atomic or molecular weight. The result so obtained is the number of molecules or atoms, which have been separated from one another during the passage into a state of vapour, and by adding one to the quotient the true amount of molecular association is obtained for the average number of molecules.

The molecular weight of solids cannot be determined in a similar manner by making use of the heat of liquefaction, because the amount of work necessary to overcome the force of cohesion or molecular dissociation cannot be determined.

The author's experimental results are arranged in three tables, the first dealing with elementary substances, the second with inorganic compounds, and the third with organic compounds. The author concludes that his numbers agree sufficiently with those obtained by previous observers to warrant the use of his method.

A. W. C.

Mutual Solubility of Liquids and the Critical Solution Point. By VICTOR ROTHMUND (*Zeit. physikal. Chem.*, 1898, 26, 433—492).—The author first gives a summary of the work of previous observers, more especially of Abascheff, Alexéeff, and Guthrie. In his own researches, he employed the synthetical method used by Alexéeff, that is, the determination of the temperatures at which mixtures of known composition become turbid on cooling and clear on heating; in almost all cases, the two temperatures lie within 0.2° , so that no supersaturation effects appear to occur. The pressure, being the vapour pressure of the liquids employed, was not constant, but the errors introduced

are quite inappreciable. For most of the pairs of liquids examined, the curves were similar to that obtained by Alexéeff for phenol and water, and the following critical temperatures were obtained; phenol-water, 68.9° ; propionitrile-water, 113.2° ; furfuran-water, 122.5° ; acetylacetone-water, 87.25° ; isobutyric acid-water, 24.3° ; hexane-methylic alcohol, 42.8° ; methylic alcohol-carbon bisulphide, 39.9° ; resorcinol-benzene, 109° . In the case of an alcoholic mixture, it is essential that the alcohol employed be absolutely free from moisture. For a mixture of methyl ethyl ketone and water, a critical temperature of about 151° was obtained, and here a minimum and maximum occur in the lower and upper branches respectively of the concentration | temperature curve so that a closed curve is indicated. With diethyl ketone and water, the critical point was not reached, but here also a minimum is found. In the case of a mixture of triethylamine and water, the author verifies Guthrie's determination of a lower critical point, that is, a temperature *below* which two liquid layers do not exist (*Phil. Mag.*, 1884). The form of the curve is normal, and differs from that given by Guthrie, which is impossible, and, contradictory to his statements. No upper critical point was reached. A lower critical point also occurs at about 6.5° in the case of β -collidine and water, and here, although the upper point was not reached, its existence was indicated by a maximum and minimum on the branches of the curve. It appears very probable, therefore, that the general form of the complete mutual solubility curve is a closed curve. If the osmotic or partial pressure of a component, and the reciprocal of its concentration, be taken as pressure and volume co-ordinates, the form of the isothermals are completely analogous to those of a liquid and its vapour, and the thermodynamics of the latter case may be applied. The diameter of the solubility curve is a straight line, that is, if C_1 , C_2 be the concentrations of a component in the two layers, then $C_1 + C_2 = A + Bt$, a further analogy to ordinary critical phenomena. The author does not find, however, that Van der Waals' law of corresponding states is obeyed, whether the concentration is calculated by weight or by volume. In the case where one of the components is a solid, its solubility curve may or may not cut the mutual solubility curve of the liquids, and only in the former case can fusion under the solvent take place. The author classifies the liquids examined with regard to the mutual solubility, and the order of the list appears to indicate some connection between this property and the dielectric constants of the liquids.

L. M. J.

Diffusion of Solids in Gases. By ALBERT COLSON (*Bull. Soc. Chim.*, 1897, [iii], 17, 164—165).—When a slow current of sulphurous anhydride is passed over lead dioxide, a deposit of lead sulphate soon makes its appearance on the walls of the tube, showing that the gas has penetrated the solid, and also that the solid has diffused through the gas. The spreading of metallic copper on the surface of the glass, when the oxide is reduced in a current of hydrogen, appears to be a phenomenon of the same kind. The experimental conditions seem to preclude the explanation of the facts by the successive formation and decomposition of easily dissociable compounds.

N. L.

Semi-permeable Membranes. By J. MIJERS (*Rec. Trav. Chim.*, 1898, 17, 177—181).—According to Ostwald, a semi-permeable membrane is both a conductor like metals [and also an “ion sieve”; experiments made by the author, however, are not in accordance with the latter idea. The copper deposited on semi-permeable membranes is not a coherent mass, but is more of a spongy nature. A glass cylinder, closed by a membrane of copper ferrocyanide on parchment paper and filled with normal copper sulphate solution, is placed in an electrolysing vessel containing the same solution, and a current from two Bunsen's elements passed through; no copper is deposited on the membrane during the first half-hour, and it is only as the liquid in the cylinder is becoming colourless that the deposit is formed. If the cathode, which is placed in the cylinder closed by the membrane, is weighed both before and after the experiment, it is found that the amount of copper deposited exceeds by a considerable amount that previously contained in the solution in the cylinder, thus indicating that copper must have passed through the membrane. If acidified water and a platinum cathode are placed in a similar cylinder closed by a membrane, and this is then placed in an electrolytic vessel containing copper sulphate, even after a few minutes metallic copper is deposited on the cathode; the amount of this copper, after 4 hours, is more than 100 times that contained in the precipitate of copper ferrocyanide on the membrane, which is not acted on by the acid and retains its colour.

Experiments have also shown that semi-permeable membranes are conductors differing entirely from metals. For example, if the anode and cathode in a copper sulphate electrolysis apparatus are separated by a semi-permeable membrane fixed between two ebonite rings and by a sheet of platinum of exactly the same size as the membrane, when the current passes, no metal is deposited on the membrane, but it is on the platinum, especially near the middle, none, however, near the margin, which is protected by the ebonite. J. J. S.

Influence of Temperature on Chemical Reactions. By ALBERT COLSON (*Compt. rend.*, 1898, 126, 1136—1138).—Although dry silver phosphate and pyrophosphate are not attacked by dry hydrogen sulphide at 0°, the action becomes distinct at 15° to 20°, and rapid at 100°. Dry zinc phosphate is not appreciably attacked between 5° and 9°, but the action becomes marked at 100°, and rapid at 160°. Experiments at 100° show that the mass of hydrogen sulphide decomposed by zinc phosphate in unit time and at a constant temperature is proportional to the square of the pressure.

Dry cupric phosphate and orthophosphate, on the other hand, absorb hydrogen sulphide slowly but continuously at 0°. The rate of the reaction is greatly reduced if the pressure is lowered, but is accelerated by a rise of temperature.

The decomposition of silver phosphate or pyrophosphate by hydrogen sulphide develops more heat than the decomposition of the corresponding cupric salts, and hence there seems to be no connection between the heat of decomposition and the temperature at which the reaction will take place. C. H. B.

Effect of Catalytic Action on the Velocity of Oxidation of Sodium Sulphite by Atmospheric Oxygen. By SAMUEL L. BIGELOW (*Zeit. physikal. Chem.*, 1898, 26, 493—532).—If a solution of sodium sulphite be oxidised by drawing through it a current of atmospheric air, the velocity of oxidation is greatly reduced by the presence of small quantities of organic compounds in the solution, and this retarding influence was examined as far as possible quantitatively. Very great difficulty was experienced in obtaining comparable results, as differences frequently occurred when the conditions were apparently identical; and although many sources of error were traced, *e.g.*, india-rubber connection in the air passages, storage of water in different vessels, yet when all those known are avoided, a series of experiments are only comparable when an initial and final experiment, under similar conditions, give the same result. Very small quantities of the catalytic agent can be then detected, thus mannitol affects the velocity when present in N/320000 solution, whilst benzaldehyde has an even more marked effect. Experiments with N/500 sodium sulphite solution, and air velocities varying from 0.5 to 4.7 litres per minute, proved that the initial velocity of oxidation is proportional to the air velocity, and that, with an exception in the case of the slowest current, the quantity of air necessary for the oxidation of 50 per cent. of the sulphite is independent of the velocity. The air velocity, however, appears to have but a slight influence when the reaction takes place in the presence of a retarding catalytic agent, so that the influence of the latter is not on the dissolution velocity of the oxygen, but on the reaction velocity $\text{Na}_2\text{SO}_3 + \text{O} \rightarrow \text{Na}_2\text{SO}_4$. With solutions of sodium sulphite of very different strengths, the curves representing concentration | time are in all cases straight lines until a concentration of about N/500 is reached, when they rapidly bend downwards, indicating a marked decrease in the velocity. This is explained by the assumption of a great velocity constant for the reaction itself, so that until the concentration is small, the oxygen is removed from solution more rapidly than it is dissolved. The retarding effect of various compounds was determined, and experiments with mannitol, ethylic alcohol, and glycerol showed that the influence is accurately additive. In the monhydric, fatty alcohols, the retardation increases slightly with the molecular weight, but this may possibly be due to their lower volatility and removal by the air current; normal and isobutylic alcohols have equal effects; that of the secondary compound is greater, and that of the tertiary almost negligible. Allylic alcohol has a greater effect than propylic alcohol, but no other comparison of saturated and unsaturated compounds was made. In the aromatic series, benzylic alcohol has an enormous effect, being the most active compound examined, its presence in N/8000 solution reducing the amount of sodium sulphite oxidised in 30 minutes from above 90 to 3 per cent.; most aromatic compounds have also great influence. The fatty aldehydes have little effect, and the ketones and ethereal salts practically none. Oxalic acid, carbonic anhydride, and ozone accelerate the velocity; sodium hydroxide has very little effect.

L. M. J.

Causes of the Reciprocal Displacements of Two Acids. By ALBERT COLSON (*Compt. rend.*, 1898, 126, 831—833).—When dry hydrogen sulphide is brought in contact with silver phosphate, the gas is at first absorbed somewhat rapidly, then more slowly, and finally a condition of equilibrium is reached in about 3 days, the pressure of the residual gas being 125 mm. at 12°; the equilibrium is not appreciably affected by increasing the pressure of the gas, but is at once disturbed by a rise of temperature. At 109°, the reaction rapidly becomes complete.

Similar phenomena were observed with silver pyrophosphate; the higher the temperature, the greater the amount of change before equilibrium is established, and the lower the pressure of the residual gas.

The reaction between a chloride and a non-volatile acid is endothermic, and that between metallic salts and hydrogen sulphide is exothermic, but in both cases a rise of temperature promotes the reaction and a fall of temperature retards it. It would seem, therefore, that temperature is the principal factor in reciprocal displacements of this kind.

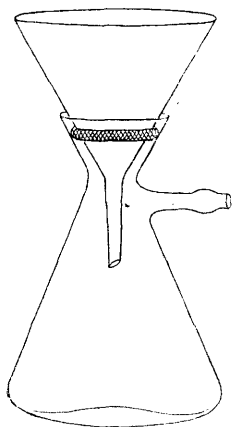
C. H. B.

A Fractionating Apparatus. By A. TIXIER, CHENAL-FERRON-DOUILHET and Co. (*Bull. Soc. Chim.*, 1897, [iii], 17, 392—395).—This somewhat complex apparatus, of which a sketch is given, consists of two parts: the analyser, formed by a bulbed tube, and the refrigerator, which is a small, subsidiary condenser. The latter effects the more or less complete condensation of the vapours from the boiling liquid, the distillation of these condensed vapours being then brought about by those subsequently formed.

N. L.

A New Filter Flask. By REINHOLD WALTHER (*J. pr. Chem.*, 1898, 57, 544—545).—The construction of this flask is easily understood from the accompanying drawing. Into the funnel-shaped neck of the flask is placed an ordinary funnel, the junction being made air-tight by means of a rubber ring, which is suitable for all sized funnels and flasks. The fitting up of the flask, as well as the removal or change of funnel, is thus much simplified.

A. W. C.

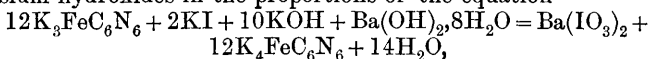


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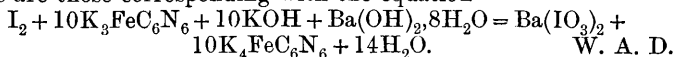
Formation of Iodates from Iodides. By GEORG KASSNER (*Arch. Pharm.*, 1898, **236**, 165—172).—Although potassium iodide is easily oxidised to iodate when warmed with nitric acid in an open vessel, it is not changed when heated with the acid in a sealed tube at

150—200°; this is accounted for by the reducing action of the nitrous acid initially produced, which is not removed from the sphere of action.

Similarly, although potassium iodide is readily converted into iodate by aqueous potassium permanganate, it remains unaffected in presence of an alkaline solution of potassium ferricyanide; this is probably due to a reverse change taking place, which involves the reduction of potassium iodate by potassium ferrocyanide. Such a change can, however, be prevented by removing the iodate as an insoluble precipitate at the moment of its formation. Thus, when a solution containing potassium iodide, potassium ferricyanide, and barium and potassium hydroxides in the proportions of the equation



is left during several hours, 75 per cent. of the iodide is oxidised, and precipitated as barium iodate; the latter, however, generally contains a considerable proportion of barium carbonate and traces of iron, but can be easily purified by washing it successively with dilute potash and nitric acid. If, in the above method, iodine is made the starting point instead of potassium iodide, the proportions which give the best results are those corresponding with the equation



Combination of Ammonium Nitrate with Ammonia. By EDWARD DIVERS (*Zeit. physikal. Chem.*, 1898, 26, 430—432).—The author had shown in 1873 (*Phil. Trans.*, 163, 359) that dry ammonium nitrate absorbs ammonia and liquefies, behaving similarly to a deliquescent salt in a moist atmosphere, and that the product may be regarded as a true solution of ammonium nitrate in ammonia. Raoult and Troost, however, considered a definite compound to be formed, and the author therefore points out that Kuriloff's recent work (this vol., ii, 156) is in complete accord with his own early investigations, and indicates the absence of any chemical compound.

L. M. J.

Action of Oxygen on Carbon Bisulphide under the Influence of Light. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 126, 1060—1066).—A mixture of air and carbon bisulphide vapour may be exposed to diffused daylight for a year without any change taking place, but if exposed to bright sunlight, some reaction takes place in an hour or two, and a yellowish-white substance is deposited which contains sulphur, carbon, and oxygen, whilst carbonic oxide and carbonic anhydride are also formed, and remain mixed with the residual oxygen and the nitrogen. No nitrogen enters into combination, and in this respect the action of light differs from that of the silent electric discharge.

The most important point about the reaction is that the light has no effect until it reaches a certain and somewhat high intensity; it is, therefore, analogous to the many reactions that do not take place below a particular temperature.

C. H. B.

Derivatives of Silicon Tetrachloride. By JOSEPH F. X. HAROLD (*J. Amer. Chem. Soc.*, 1898, 20, 13—29).—The author finds that silicon tetrachloride does not act on the following substances, formonitrile, acetonitrile, propionitrile, succinonitrile, benzonitrile, toluonitrile, nitric peroxide, the mixed vapours of nitric peroxide and chlorine, the chlorides of phosphorus, sulphur monochloride, or cyanogen chloride. When silicon tetrachloride is heated with mandelonitrile or lactonitrile, silicic acid and complex tarry products are formed. By the action of aniline (4 mols.) on silicon tetrachloride (1 mol.) dichlorosilicondianilide, $\text{SiCl}_2(\text{NHPh})_2$, and aniline hydrochloride are obtained. The violence of the action is moderated by using anhydrous ether or benzene; in the former case, both products are precipitated; in the latter, the silicon compound remains in solution. According to the author, in the longer and less direct method of Reynolds (*Trans.*, 1889, 55, 474) a further reaction between dichlorosilicondianilide (1 mol.) and aniline (4 mols.) takes place, whereby silicontetranilide, and aniline hydrochloride are formed. Silicon tetrachloride acts on orthotoluidine more readily than on aniline, the action taking place even in a freezing mixture, the products being analogous to those obtained in the case of aniline. When silicon tetrachloride vapour is passed into molten benzamide, benzaldehyde is formed, whilst with acetamide, the tetrachloride yields acetonitrile.

E. W. W.

Method of Preparing Metals and Alloys by means of Aluminium. By HANS GOLDSCHMIDT (*Annalen*, 1898, 301, 19—28).—Since the discovery of a method of preparing aluminium in large quantities, advantage has been taken of the reducing action of this metal towards metallic chlorides and oxides. In many cases, the action is so violent that only small quantities of material can be dealt with conveniently. By avoiding the application of external heat, however, the author has found that the change may be kept under control, sufficient heat to start the interaction being supplied at a point in the mixture by means of ignited magnesium ribbon. The best results are achieved when several kilograms of material are manipulated at one time.

In this way, a large number of metals, even those which are not readily fusible, may be prepared without difficulty; if a small excess of the oxide is employed, the metal is obtained uncontaminated with aluminium. Chromium and manganese have been prepared in a very pure condition; the latter metal exhibits surface colours, and has greater cohesive power than when produced by the ordinary method.

The sulphides of the metals may be advantageously used in place of the oxides; in this case, the temperature of reaction is lower.

M. O. F.

Metallic Precipitation. By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1897, [iii], 17, 271—286. Compare *Abstr.*, 1897, ii, 171, 319, and 448).—The action of metals on solutions of metallic nitrates having been dealt with in former communications, the author now gives the results of further experiments on the action of various metals on the sulphates, chlorides, and acetates of silver, copper, and lead. The

substances used were chemically pure, and the experiments were carried out in neutral solutions at the ordinary temperature, with exclusion of air.

The nature of the acid radicle of the salt appears to exercise a marked influence on the precipitation. Thus, tin and iron precipitate silver and copper from their sulphates, but have no action on the acetates; bismuth, on the other hand, precipitates silver acetate, but not the sulphate. Aluminium completely precipitates silver sulphate, but has scarcely any action on silver acetate; it acts rapidly on cupric chloride, very slowly on cupric sulphate, and still more slowly on the acetate. In many cases, the rapidity and character of the precipitation varies with the concentration of the solution. It is remarkable that nickel has no action on the salts examined, with the exception of a very limited reaction in the case of cupric chloride, whereas cobalt brings about immediate precipitation.

As a general rule, the amount of the precipitating metal which enters into reaction is greater than that accounted for by the equation $R''SO_4 + M'' = M''SO_4 + R''$, owing to the occurrence of various secondary reactions. Sometimes, as with zinc and aluminium, hydrogen is evolved and the precipitating metal is converted into a basic salt; sometimes, as in the cases of tin and bismuth, an acid salt remains in solution whilst an oxide or a basic salt is precipitated. In almost every case, the precipitated metal is contaminated more or less with the precipitating metal, a definite alloy being formed by the action of cadmium on silver salts (this vol., ii, 25). Zinc alone, acting on a solution of lead acetate, appears to give a precipitate of pure metal.

N. L.

Action of Calcium Sulphate on Halogen Alkali Salts. By ALFRED DITTE (*Compt. rend.*, 1898, 126, 694—700).—In dilute solutions, the decomposition of calcium chloride by alkali sulphates would be slightly endothermic (-0.9 Cal.), and hence, under these conditions, calcium sulphate should decompose alkali chlorides.

When calcium chloride and potassium sulphate solution interact in presence of potassium chloride solution, there is no apparent change so long as the proportion of calcium chloride remains below a certain limit, but if this limit is exceeded, slender, transparent, brilliant needles of the double sulphate, $CaSO_4 \cdot K_2SO_4 + 4H_2O$, are gradually deposited. It is obvious that the formation of this double salt may serve to change the thermal sign of the reaction. The salt readily forms supersaturated solutions; analyses of the solution after equilibrium has been attained consequent on each fresh addition of calcium chloride show that the higher the proportion of calcium remaining in the solution, the lower the proportion of sulphuric acid, and *vice versa*. Numbers are given showing the conditions of equilibrium at 24° in a solution containing 120 grams of potassium chloride per litre.

On the other hand, when calcium sulphate is in contact with potassium chloride solutions of increasing concentration, the proportions of calcium and sulphuric acid dissolved at first increase with the quantity of potassium chloride, and the relative proportions indicate that the calcium sulphate dissolves unchanged. Beyond a certain point, however

the quantity of calcium dissolved continues to increase, but the quantity of sulphuric acid dissolved reaches a maximum and then decreases; at the same time, the crystals of the double sulphate gradually separate. If the quantities of potassium chloride are represented by the abscissæ, and the quantities of either calcium or sulphuric acid in the solution are represented by ordinates, regular curves are obtained, that of the calcium being first concave and afterwards convex towards the horizontal axis. The curve of sulphuric acid reaches a maximum and then descends, the points of inflexion of the two curves falling on the same ordinate. It is clear, therefore, that, whilst under certain conditions potassium sulphate can decompose calcium chloride, under other conditions the reverse change takes place and the formation of the double sulphate, and the proportion of potassium chloride present, are important factors in the establishment of equilibrium.

With potassium or calcium bromide, the phenomena are practically the same as with the respective chlorides, and the iodides behave similarly.

With ammonium chloride and sodium chloride, the results are also similar, except that no formation of a double sulphate takes place.

C. H. B.

Action of Strontium Chromate on Mercuric Chloride. By H. IMBERT and G. BELUGOU (*Bull. Soc. Chim.*, 1897, [iii], 17, 471—473).—One hundred and two grams of strontium chromate are dissolved in 50 c.c. of concentrated hydrochloric acid, and the solution diluted with water to 250 c.c.; 271 grams of mercuric chloride are then dissolved in the liquid, which is warmed on the water bath, filtered, and allowed to cool. Orange-red crystals separate, which, on drying over sulphuric acid, have the composition $\text{SrCrO}_4 \cdot 2\text{HgCl}_2 \cdot \text{HCl}$. The compound is not decomposed by water.

N. L.

Action of Strontium Chromate on Mercuric Chloride. By G. BELUGOU (*Bull. Soc. Chim.*, 1897, [iii], 17, 473—474).—20.4 grams of strontium chromate, 27.1 grams of mercuric chloride, and 200 c.c. of water are heated together on the water bath, the liquid being finally filtered from the insoluble reddish residue, which probably contains basic mercuric chromate. The filtrate, on cooling, deposits orange-yellow crystals, which, when dried over sulphuric acid, have the composition $2(\text{SrCrO}_4 \cdot 3\text{HgCl}_2) \cdot \text{HCl}$.

N. L.

Dissociation of Barium and Manganese Carbides. By GIN and LELEUX (*Compt. rend.*, 1898, 126, 749—750).—When barium or manganese carbide is heated in an electric furnace with a current of 35 volts and 16 ampères per sq. cm., it dissociates into the metal, which volatilises, and carbon which remains in the form of graphite. The barium compound dissociates more readily than the manganese compound, but both decompose below the volatilising point of carbon. (Compare this vol., ii, 322.)

C. H. B.

Preparation of Beryllium by Electrolysis. By PAUL LEBEAU (*Compt. rend.*, 1898, 126, 744—746).—Beryllium fluoride, like the other haloid salts, is a non-conductor of electricity when fused, but becomes a conductor and electrolyte when mixed with an alkali

fluoride. The beryllium sodium fluorides, $\text{BeF}, 2\text{NaF}$ and BeF, NaF , are most readily prepared by dissolving the necessary quantities of beryllium hydroxide and sodium carbonate in hydrofluoric acid; the first melts at about 350° , and the second at a red heat. The fused salt is electrolysed in a nickel crucible, which serves as the cathode, whilst the anode is a rod of graphitic carbon. When the current passes, the source of heat is withdrawn; the salt remains fused, and it is important that the temperature should never exceed an incipient red heat. A current of 6 to 7 ampères and 35 to 40 volts is sufficient, and the metal separates in a crystalline form.

Alloys of beryllium can be obtained by conducting the electrolysis in a carbon crucible, which serves as the anode, and contains the other metal in a state of fusion. C. H. B.

Attempts to prepare Hydrated Double Chloride or Bromide of Sodium and Magnesium. By AUGUSTE DE SCHULTEN (*Bull. Soc. Chim.*, 1897, [iii], 17, 169—170).—Attempts to prepare the double chloride, $\text{NaCl}, \text{MgCl}_2 + \text{H}_2\text{O}$, described by Poggiale, were unsuccessful. The corresponding double bromide also appears to be incapable of existence. N. L.

Production of Brominated Potassium and Ammonium Carnallites. By A. DE SCHULTEN (*Bull. Soc. Chim.*, 1897, [iii], 17, 167—169).—Substituted carnallites of the formulæ $\text{KBr}, \text{MgBr}_2 + 6\text{H}_2\text{O}$ and $\text{NH}_4\text{Br}, \text{MgBr}_2 + 6\text{H}_2\text{O}$ are formed when solutions of the mixed salts are slowly evaporated over sulphuric acid; a large excess of the magnesium salt must, however, be employed. The crystallographic characters and optical properties of the salts are described. The double salt obtained by Löwig, and stated by him to have the formula $2\text{KBr}, \text{MgBr}_2 + 6\text{H}_2\text{O}$, could not be prepared; nor could the corresponding double chloride. The product obtained by Löwig was probably a mixture of potassium bromide with brominated carnallite. N. L.

Attempts to Produce Compounds Isomorphous with Kainite and with Tachyhydrite. By A. DE SCHULTEN (*Bull. Soc. Chim.*, 1897, [iii], 17, 165—167).—Experiments were made with a view to ascertain whether the methods which have been successfully employed for the synthesis of kainite, $\text{K}_2\text{SO}_4, \text{MgSO}_4, \text{MgCl}_2 + 6\text{H}_2\text{O}$, and tachyhydrite, $\text{CaCl}_2, 2\text{MgCl}_2 + 12\text{H}_2\text{O}$, could be used for the production of isomorphous compounds of the formulæ $(\text{NH}_4)_2\text{SO}_4, \text{MgSO}_4, \text{MgCl}_2 + 6\text{H}_2\text{O}$, $\text{K}_2\text{SO}_4, \text{MgSO}_4, \text{MgBr}_2 + 6\text{H}_2\text{O}$, and $\text{CaBr}_2, 2\text{MgBr}_2 + 12\text{H}_2\text{O}$. Such compounds appear, however, to have no existence. N. L.

Double Haloid Salts of Lead and Ammonium. By H. FONZES-DIACON (*Bull. Soc. Chim.*, 1897, [iii], 17, 346—356).—According to Rensen, the number of molecules of an alkali haloid which combines with a molecule of a metallic haloid is never greater, and is usually less, than the number of halogen atoms contained in the latter. It is admitted, however, that the compounds containing ammonium haloids often form exceptions to this rule, and, not being satisfied with the explanations of this fact usually offered, the author has made a complete study of all the compounds to be obtained by

the action of solutions of ammonium haloids on lead haloids. The latter are dissolved by hot solutions of the ammonium salts, and, on cooling, the solutions deposit the double salts, the composition of which depends on the experimental conditions. Since these compounds undergo dissociation in aqueous solution, the crystals must be washed with a dilute solution of the ammonium haloid used in their preparation. The analysis of these salts is carried out as follows: the lead is converted into lead sulphate, ammonium sulphate being expelled by heating to redness; the ammonia is distilled and titrated; the halogens are calculated from the weight of mixed silver salts into which they are converted, combined with a volumetric determination of the amount of silver required to combine with them. The following new compounds are described.

Salts of the type MX_3A .— $\text{Pb}(\text{ClI}_2)\text{NH}_4 + 2\text{H}_2\text{O}$; $\text{Pb}(\text{BrI}_2)\text{NH}_4 + 2\text{H}_2\text{O}$.

Salts of the type MX_4A_2 .— $\text{Pb}(\text{Cl}_2\text{Br}_2)(\text{NH}_4)_2 + 4\text{H}_2\text{O}$; $\text{PbBr}_4(\text{NH}_4)_2$.

Salts of the type $\text{M}_2\text{X}_5\text{A}$.— $\text{Pb}_2(\text{Cl}_4\text{Br})\text{NH}_4$; $\text{Pb}_2(\text{Br}_4\text{Cl})\text{NH}_4$; $\text{Pb}_2\text{Br}_5\text{NH}_4$; $\text{Pb}_2(\text{BrI}_4)\text{NH}_4$.

Salt of the type $\text{M}_3\text{X}_{10}\text{A}_4$.— $\text{Pb}_3\text{I}_{10}(\text{NH}_4)_4 + 6\text{H}_2\text{O}$.

No double fluoride could be prepared; the action of ammonium bromide on lead fluoride gave rise to the compound PbFBr , analogous to the compound PbFCl previously obtained by Berzélius.

All these substances are well-defined crystalline compounds which are decomposed by water, but are dissolved by caustic potash and by strong acids. In every case, Remsen's law holds good, and no evidence could be found for the existence of the complex salts, probably mixtures, described by Woelckel, Poggiale, and André, and which have been cited as exceptions to the law. N. L.

Double Thiosulphates of Copper and Potassium. By WILHELM MUTHMANN and L. STÜTZEL (*Ber.*, 1898, 31, 1732—1735).—*Potassium cuprithiosulphate*, $\text{Cu}(\text{S}\cdot\text{SO}_3\text{K})_2$, is obtained by mixing solutions of potassium thiosulphate and copper sulphate, the blue colour of the latter salt being changed to pale yellow; it forms slender, colourless needles, and if allowed to remain in contact with the mother liquor for several days, becomes brown from the separation of cupric sulphide. The salt is probably identical with the compound described by Cohen (*Trans.*, 1897, 51, 38), who gave to it the formula $\text{Cu}_2\text{S}_2\text{O}_3\cdot 2\text{K}_2\text{S}_2\text{O}_3$; apart from analysis, however, its behaviour accords more closely with that of a cupric compound. Caustic soda produces a very faint turbidity in the aqueous solution, whilst the solid substance, on digestion with the agent, yields black copper oxide; potassium ferrocyanide gives the characteristic reddish-brown cupric ferrocyanide, and hydrogen sulphide produces colloidal cupric sulphide, which is precipitated by acids and neutral salts. From the behaviour of the salt towards caustic soda and ammonia, which does not develop colour, the authors regard it as having the above constitution, rather than that of a double salt.

Potassium cuprithiosulphate crystallises in beautiful, yellow prisms, having the composition $\text{Cu}_2\text{S}_2\text{O}_3\cdot 2\text{K}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O}$; recrystallisation from water yields a tetrahydrate differing in crystalline form from the

dihydrate. The cuprous salt described by Cohen (*loc. cit.*) is probably a mixture of these hydrates. The solution is intensely yellow, and gives the reactions of a cuprous salt. M. O. F.

Cuprosammonium Bromides and Cuprammonium Thiocyanates. By THEODORE W. RICHARDS and BENJAMIN S. MERIGOLD (*Zeit. anorg. Chem.*, 1898, 17, 245—252).—*Cuprosammonium bromide*, $\text{Cu}_2\text{Br}_2(\text{NH}_3)_2$, is obtained by dissolving cuprous bromide (10 grams) in the least possible quantity of ammonia, and adding acetic acid (25 c.c), the crystalline product being washed with alcohol and ether, and dried over sulphuric acid under diminished pressure; all the operations must be carried out in an atmosphere of hydrogen. It crystallises in long, flat, colourless prisms, is quite stable when dry, but quickly oxidises when exposed to the air in contact with water, and is easily soluble in ammonia and nitric acid.

Cuprosammonio-thiocyanate, $\text{Cu}_2(\text{NH}_3)_2(\text{SCN})_2$, obtained by adding ammonium thiocyanate to a solution of cuprous hydroxide in ammonia, is a white, crystalline powder which quickly loses ammonia on exposure to the air.

Tetrammonio-cuprosammonium bromide, $\text{Cu}_2\text{Br}_2(\text{NH}_3)_6(?)$, is obtained by saturating finely powdered cuprous bromide, cooled with ice, with dry ammonia; it is a black powder, decomposed by water, and soluble in ammonia and nitric acid. It is extremely unstable, and easily gives off its ammonia.

Triammonio-cuprosammonium thiocyanate, $\text{Cu}_2(\text{NH}_3)_5(\text{SCN})_2$, obtained by saturating powdered cuprous thiocyanate with dry ammonia, is a black powder which is very unstable, and quickly gives off ammonia on exposure to the air.

Diammonio-cuprammonium thiocyanate, $\text{Cu}(\text{SCN})_2(\text{NH}_3)_4$, is obtained by adding ammonium thiocyanate to a solution of cuprammonium bromide, and then adding sufficient ammonia to dissolve the precipitate which is produced; the new compound soon separates from this solution in lustrous, deep-blue crystals. It gives off ammonia on exposure to the air, is decomposed by water and dilute acids, and is soluble in hot concentrated hydrochloric acid, in cold concentrated nitric acid, and in ammonia. E. C. R.

Colloidal Silver. II. By ALFRED LOTTERMOSER and ERNST VON MEYER (*J. pr. Chem.*, 1898, [ii], 57, 540—543. Compare this vol., ii, 116).—In order to study the influence of time on the change of colloidal to molecular silver, a certain amount of acid was added in one portion to a solution of colloidal silver, and the time necessary for the complete change observed; the end of the reaction is easily determined by placing a drop of the solution on a glass plate, and looking through this on to white paper; as soon as the separation of fine silver particles could be clearly seen, the time was noted.

The results of experiments which are tabulated show that the less the amount of acid used, the longer the time necessary for the reaction; and the amount of acid which will produce the change in a certain time stands in inverse proportion to the concentration of the solution.

In continuation of their work on the precipitation of colloidal silver

by salts of the heavy metals, the authors show that in the case of reducible metallic chlorides, silver chloride and the lower chloride of the metal are formed; a part of the silver is, however, always precipitated in the insoluble form. If both solutions (colloidal silver and metallic chloride) are very dilute, it often happens that neither silver chloride nor the lower chloride of the metal are precipitated but remain in solution in the colloidal form; particularly is this the case with mercuric chloride.

Colloidal silver iodide appears to be of therapeutic interest, but, like colloidal silver chloride and bromide, has no use in photography.

A. W. C.

Ammonio-Silver Bromides. By R. JARRY (*Compt. rend.*, 1898, 126, 1138—1142).—Dry silver bromide is converted by liquefied ammonia into a white powder, which at 4° loses a large quantity of ammonia, and at about $+35^{\circ}$ loses a second quantity of the gas, a residue of yellow silver bromide being left. The compound stable below 4° has the composition $\text{AgBr}\cdot 3\text{NH}_3$, whilst that stable up to 35° has the composition $2\text{AgBr}\cdot 3\text{NH}_3$, the two being analogous respectively to the ammonio-silver chlorides (*Abstr.*, 1897, ii, 259). Their dissociation pressures are as follows.

$\text{AgBr}\cdot 3\text{NH}_3$.									
t°	-23°	-18°	-8°	0°	$3\cdot 5^{\circ}$	$8\cdot 0^{\circ}$	14°	20°	23°
p	14	19\cdot 5	36	60\cdot 5	74\cdot 5	92	131	182	214 mm.

$2\text{AgBr}\cdot 3\text{NH}_3$.									
t°	0°	4°	$10\cdot 4^{\circ}$	$11\cdot 2^{\circ}$	14°	$16\cdot 6^{\circ}$	$28\cdot 6^{\circ}$	$43\cdot 8^{\circ}$	53°
p	8\cdot 8	10\cdot 7	16\cdot 6	17\cdot 4	20\cdot 6	24\cdot 9	51\cdot 3	122\cdot 5	198\cdot 6 mm.

The absorption of gaseous ammonia by silver bromide, even at -20° , is very slow, and this probably explains Rammelsberg's statement that no absorption takes place. Liquefied ammonia dissolves a small quantity of the compound $\text{AgBr}\cdot 3\text{NH}_3$, and deposits it in transparent, birefractive needles when allowed to evaporate. The compound $2\text{AgBr}\cdot 3\text{NH}_3$ is likewise obtained in small needles by allowing a solution of silver bromide in ordinary ammonia to evaporate over potash or lime in an atmosphere of ammonia. Highly concentrated ammonia solution, in contact with silver bromide, seems to convert it into the compound $\text{AgBr}\cdot 3\text{NH}_3$, which, however, is decomposed on dilution, whilst the second compound is decomposed on further dilution.

The solubility of silver bromide at 0° , in 10 c.c. of ammonia solution of various strengths, is as follows.

NH_3 . Gr.	AgBr . Mgr.	NH_3 . Gr.	AgBr . Mgr.	NH_3 . Gr.	AgBr . Mgr.	NH_3 . Gr.	AgBr . Mgr.
0\cdot 307	8\cdot 0	1\cdot 151	34\cdot 9	2\cdot 627	106\cdot 7	3\cdot 722	288\cdot 8
0\cdot 488	9\cdot 6	1\cdot 532	55\cdot 7	3\cdot 126	156\cdot 8	3\cdot 770	293\cdot 0
0\cdot 669	17\cdot 2	1\cdot 809	72\cdot 2	3\cdot 389	198\cdot 7	3\cdot 926	289\cdot 2
0\cdot 829	21\cdot 2	1\cdot 953	74\cdot 1	3\cdot 652	266\cdot 9	3\cdot 995	285\cdot 0

The curve representing these results shows two breaks corresponding with solutions saturated under the dissociation pressures of the two compounds $\text{AgBr}\cdot 3\text{NH}_3$ and $2\text{AgBr}\cdot 3\text{NH}_2$ respectively, the three

sections of the curve, therefore, representing, first, the solubility of silver bromide; secondly, the solubility of the compound $2\text{AgBr}, 3\text{NH}_3$, and lastly, the solubility of the compound $\text{AgBr}, 3\text{NH}_3$. The two compounds form and dissociate in ammonia solution, just as they do in a vacuum.

C. H. B.

Silver Peroxynitrate and Silver Peroxide. By EDUARD MULDER (*Rec. Trav. Chim.*, 1898, 17, 129—176. Compare Abstr., 1896, ii, 561; 1897, ii, 260 and 551).—When the compound $\text{Ag}_7\text{NO}_{11}$ is deprived of an atom of oxygen and the product extracted with water, silver nitrate passes into solution, and silver peroxide, Ag_2O_2 , is left. The silver nitrate can be extracted in a short time, and it is suggested that the compound $\text{Ag}_7\text{NO}_{11}$ has the composition $3\text{Ag}_2\text{O}_2, \text{AgNO}_5$. When the peroxynitrate is boiled with water, oxygen is liberated, silver nitrate goes into solution, and a residue of silver peroxide is obtained. This is the most convenient method for the preparation of the peroxide on a fairly large scale.

The peroxide dissolves in either concentrated nitric or sulphuric acid, yielding brown solutions; decomposition is facilitated by the presence of water. Acetic acid itself does not dissolve the peroxide, but in presence of water, silver acetate, water, and oxygen are obtained. The author gives a list of silver peroxides which have been described by different authorities.

A method for estimating the oxygen excess in the peroxynitrate is described; it is based on the decomposition of the compound with water. The peroxynitrate undergoes slow, spontaneous decomposition when kept for any length of time, even over sulphuric acid, the decomposition is so slow, however, that it would require about 13 years for the two atoms of oxygen (oxygen excess) to be eliminated.

J. J. S.

Amalgams. By WILHELM KERP (*Zeit. anorg. Chem.*, 1898, 17, 284—309).—Sodium amalgam containing 2.5—3 per cent. of sodium was prepared by melting sodium with mercury. When this solid amalgam is dissolved in warm mercury and the solution allowed to cool, a crystalline amalgam separates when the solution contains 0.7 per cent. or more of sodium; the author has determined the composition of the crystals and the mother liquor obtained by dissolving known weights of the solid amalgam in mercury at known temperatures. The mixture of amalgam and mercury is placed in a sealed tube and shaken in a thermostat, and when the solution is complete, the crystals are separated by filtration with the aid of an air pump through a leather dish arranged in a Gooch's crucible. The sodium in the amalgam is estimated by treating a weighed portion with an excess of $\text{N}/2$ hydrochloric acid and determining the excess of acid with barium hydroxide solution, using "ethyl-orange" as indicator.

At temperatures from 0° to 100° , the crystalline amalgam has the composition NaHg_5 , and all the mother liquors separated at 25° and above deposited the same compound on cooling; the percentage of sodium in the mother liquors varies from 0.544 at 0° to 1.10 at 99.8° . The solubility of sodium in mercury is, therefore, very small, and is comparable with that of potassium, barium, and strontium; thus 100

parts of amalgam at 0° contain 0.25 parts K, 0.544Na, 0.17 Ba, and at the ordinary temperature 0.45K, 0.643Na, 0.33Ba, and 0.90—1.00 parts Sr. It is remarkable that sodium is more soluble than potassium, and strontium than barium. Sodium amalgam has no definite melting point, it begins to soften at 105° , is converted into a fluid magma at 119° , and is completely molten at 138 — 139° ; on allowing the mass to cool, crystals begin to form at 137° , at 128° it is full of beautiful needles, and is completely solid at 103° . This behaviour indicates the formation of a more concentrated amalgam above 100° , and shows that the solubility of sodium increases rapidly above 100° , since the amalgam which melts at 138° must contain at least 2.25 per cent. of sodium.

Potassium amalgam was obtained by the electrolysis of a solution of potassium chloride, using a mercury cathode. The apparatus, which is fully described in the paper, is so arranged that the mercury can be passed through the potassium chloride several times, and the mixture of solid and liquid amalgam is collected in an atmosphere of hydrogen. The crystals are separated from the mother liquor by filtration in the same way as described above for sodium amalgam. The larger crystals must be completely broken up, as they are very porous and absorb large quantities of the mother liquor. The amalgam crystallises in large, silvery cubes truncated by octahedral and dodecahedral faces, and has the composition KHg_{12} .

Barium amalgam, which can be very easily obtained in a similar manner to potassium amalgam, by the electrolysis of a saturated solution of barium chloride, crystallises in small, hard, lustrous cubes, and has the composition BaHg_{12} when prepared between 21° and 81° . The mother liquor contains, at 0° , 0.160 to 0.178 per cent. of barium, and at 81° , 0.969 per cent. The amalgam is very easily oxidised on exposure to the air, and cannot, therefore, be fused in the air; it is, however, very slowly attacked by water, and oxidised samples can be purified by washing with water.

Strontium amalgam, obtained by the electrolysis of a saturated solution of strontium chloride, is somewhat difficult to prepare on account of the ease with which it is attacked by water; during the electrolysis large quantities of hydrogen are evolved, and the solution of strontium chloride quickly becomes saturated with strontium chlorate. The amalgam separates in very slender crystals, and is quickly oxidised on exposure to the air. When crystallised at the ordinary temperature, it has the composition SrHg_{11} , when crystallised at 64 — 81° , the composition SrHg_8 .

Sodium amalgam containing 0.685 per cent. sodium is very slowly decomposed by water or N/10 solutions of sodium chloride, carbonate, or pure hydroxide; with the ordinary pure sodium hydroxide of commerce, however, the decomposition is very rapid, being for N/4 solutions 40 times as great as with water, and for N/10 solutions 5 times as great. This increase in the rapidity of the decomposition is due to traces of silica, iron, zinc, and aluminium, and when a small quantity of the hydroxide of a metal which is soluble in sodium hydroxide is added to a solution of pure sodium hydroxide, the rate of decomposition of the amalgam is greatly increased. E. C. R.

New Method of Fractionating Metals of the Yttrium Group. By G. URBAIN (*Compt. rend.*, 1898, 126, 835—838).—The ethyl sulphates of the metals of the yttrium group, which are easily prepared by the interaction of barium ethyl sulphate and the sulphate of the particular metal, crystallise very readily. These facts can be utilised for the separation, by fractional crystallisation, of the various metals, which crystallise in the following order : yttrium, terbium, holmium, and dysprosium, erbium, ytterbium. C. H. B.

Separation of the Cerite Metals : Solubility of their Sulphates in Water. By WILHELM MUTHMANN and H. RÖLIG (*Ber.*, 1898, 31, 1718—1731. Compare this vol., ii, 376).—The authors describe a series of experiments undertaken with the object of devising a method of separating the cerite metals. They have obtained the enneahydrate of lanthanum sulphate, the octo- and penta-hydrates of praseodymium sulphates, and the octohydrate of neodymium sulphate ; the solubilities of these salts in water have been determined, and the appropriate curves are given in the original paper.

M. O. F.

Neodymium. By O. BOUDOUARD (*Compt. rend.*, 1898, 126, 900—901).—Neodymium can be isolated by allowing a solution of the pure sulphates of the yttrium metals to remain in contact with excess of potassium sulphate for at least 24 hours, decomposing the insoluble double sulphate with sodium hydroxide, dissolving the oxide thus obtained in nitric acid, and precipitating with oxalic acid. The metal thus isolated has the atomic weight 143, which agrees closely with the value 142.7 obtained in previous experiments. The oxide is greenish, the oxalate and anhydrous sulphate are slightly rose-coloured ; the crystallised sulphate, which is rose-coloured, is less soluble than the anhydrous sulphate, and is more soluble in cold water than in hot.

The absorption spectrum of the sulphate of this metal is as follows : 591.5 to 584, shadow ; 584—572, intense band ; 523—519, intense band ; 512—508, feeble band ; 480 and 470, faint bands, probably due to traces of praseodymium.

It is noteworthy that neodymium forms a double sulphate with potassium more soluble than the praseodymium compound.

C. H. B.

Spectrum and Elementary Nature of Neodymium. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1898, 126, 1039—1041).—Didymium oxide, carefully purified from lanthanum and cerium, and fractionated by Auer von Welsbach's method of ammoniacal nitrates, yielded neodymium free from samarium and praseodymium. Repeated fractionation by the method indicated, and also by other methods, failed to produce any alteration in the spectrum, and it follows that neodymium is an elementary body and not a mixture of two or more substances as has been asserted.

Neodymium oxide prepared from the oxalate has, contrary to the statements of other observers, a pale bright blue colour, which is distinctly altered by very small quantities of praseodymium, samarium, or terbium. The colour of its salts varies, according to the concen-

tration of the solution, from lilac blue to reddish-violet, but in presence of small quantities of samarium or praseodymium compounds the colour is a yellowish- or brownish-red.

An acid solution of the chloride shows the following bands: 7324, 6910, 6804 (strong), 6731 (feeble), 6373, 6292 (double and very feeble), 6234, 5783 (about the middle of the very strong band), 5220 (about the middle of the strong band), 5320 (fairly strong), 5109 (very strong in the middle), 4768 (strong), 4691 (strong), 4624 (nebulous and diffuse, but fairly strong), 4351 (feeble), 4294 (very feeble), 4281 (strong), 4200 (very feeble).

The bands below 5109 are rendered very faint and indistinct by the presence of a certain quantity of samarium, and this may explain why they have not been observed by other investigators. Some of the bands are greatly affected by variations in the nature of the acid; the small group about 6300, for example, is very difficult to recognise in presence of nitric acid.

C. H. B.

Praseodymium. By CARL VON SCHELE (*Zeit. anorg. Chem.*, 1898, 17, 310—326).—The praseodymium compounds are obtained as follows. Monazite sand is decomposed by sulphuric acid, the aqueous solution precipitated with oxalic acid, and the washed precipitate dried at 100° and dissolved in concentrated nitric acid. The cerium and thorium salts are separated by repeatedly evaporating the solution, and the solution containing the other oxides is mixed with ammonium nitrate and subjected to fractional crystallisation according to Welsbach's method. The praseodymium salts collect in the fractions between the lanthanum and didymium fractions. The fractions richest in praseodymium are then mixed with sodium nitrate and fractionally crystallised; of these, the fractions which contain neodymium are converted into the double salt with ammonium nitrate mixed with cerium ammonium nitrate, and fractionally crystallised, when the praseodymium accompanies the cerium salt and the neodymium remains in the mother liquors. The product thus obtained is free from neodymium, and contains only a trace of lanthanum. It is boiled with ammonium nitrate, which dissolves any sesquioxides, and the peroxide is finally converted into the oxalate and fractionally crystallised from nitric acid. The author, on subjecting the product to fractional crystallisation from ammonium nitrate and examining the different fractions spectroscopically, was unable to detect the presence of any other element in the praseodymium except a trace of lanthanum.

Praseodymium yields two oxides, namely, Pr_2O_3 which is green, and PrO_2 , which is black; only the first of these is capable of forming salts. The atomic weight was determined as follows: the oxalate was converted into the peroxide by heating at a red heat, the peroxide reduced to oxide by heating in a platinum boat in a current of hydrogen at a white heat, and then the weight of the sulphate obtained from a known weight of oxide was determined. The mean of five determinations gave 140.40 (O = 16, S = 32).

Praseodymium peroxide, PrO_2 is a black, lustrous powder obtained by heating praseodymium salts in the air or in a current of oxygen. When strongly heated, it gives off oxygen, and is converted into the

green oxide; it yields chlorine when treated with hydrochloric acid, and oxygen when treated with other acids. When treated with ferrous ammonium sulphate, or with an acid solution of stannous chloride, part of the oxygen escapes without oxidising the ferrous or stannous salt. The analysis of the oxide can, however, be effected by heating it at a high temperature in a current of hydrogen.

Praseodymium oxide, Pr_2O_3 , obtained by reducing the peroxide, is very similar to lanthanum oxide. It absorbs carbonic acid from the atmosphere, and is converted into the peroxide when heated in the air or when fused with potassium chlorate. The sp. gr. = 6.881.

E. C. R.

Synthesis of Crystalline Alumina by the Action of Chlorine on an Alkali Aluminate. By H. LOYER (*Bull. Soc. Chim.*, 1897, [iii], 17, 345—346).—When a slow current of chlorine is passed through a heated porcelain tube containing potassium or sodium aluminate mixed with 1 per cent. of potassium chromate, oxygen is evolved, and a rose-coloured, crystalline mass is formed. This consists, for the most part, of well-defined hexagonal crystals, like those of the ruby, which are insoluble in hydrochloric and nitric acids, and sink in methylenic iodide.

N. L.

Water of Crystallisation of Manganous Sulphate. By W. SCHIEBER (*Monatsh.*, 1898, 19, 280—297).—Manganous sulphate separates from an aqueous solution below 0° as the heptahydrate, between 15° and 20° as the pentahydrate, between 25° and 31° as the rhombic tetrahydrate, and between 35° and 40° as a mixture of the rhombic and monoclinic tetrahydrates; all these hydrates, on warming to 55° or on standing for some days over sulphuric acid, become converted into the monohydrate.

The hexa-, tri-, and di-hydrates do not exist.

G. T. M.

Tetrahydrated Oxide of Iron. By WALTHER SPRING (*Rec. Trav. Chim.*, 1898, 17, 222—223).—If the voluminous precipitate obtained by the addition of ammonia to a dilute solution of ferric chloride or sulphate is dried spontaneously at the ordinary temperature, a vitreous substance is obtained, which is black in mass but red by transmitted light. It has the composition $\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$. Placed in a desiccator, it loses water; its sp. gr. = 2.436 at 15° , and it is not decomposed by pressure.

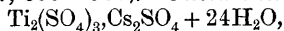
J. J. S.

A New Chromium Silicide. By CH. ZETTEL (*Compt. rend.*, 1898, 126, 833—835).—When a mixture of 140 parts of copper and 140 parts of aluminium is melted in a fire-clay crucible and 200 parts of chromic oxide, previously strongly heated, is added gradually, and after strongly heating for some time, a small quantity of aluminium filings, there is a very energetic action. The metallic ingot obtained on cooling contains crystals of a chromium silicide, SiCr_3 , which is separated from the metal by the action of aqua regia. It is not attacked by any acids with the exception of hydrofluoric acid, but chlorine and bromine decompose it at a red heat. Sulphur has no action at dull redness, and fused potassium chlorate attacks the silicide with difficulty even at a red heat. Fused potassium hydroxide

attacks it slowly, but a fused mixture of alkali nitrates and carbonates decomposes it rapidly. The crystals scratch glass but not quartz; sp. gr. = 6.52 at 18°. C. H. B.

Tungsten Iodide. By ED. DEFACQZ (*Compt. rend.*, 1898, 126, 962—974).—When hydrogen iodide acts on sublimed tungsten hexachloride at about 400°, tungsten di-iodide, WI_2 , is obtained as an amorphous, brown powder of sp. gr. 6.9 at 18°, and insoluble in water, alcohol, or carbon bisulphide. It is infusible and non-volatile; when heated in air, it is oxidised, and when heated above 500° in hydrogen it is reduced. Chlorine decomposes it at about 250°, and bromine at about 350°. Hydrogen iodide reduces it at 500—600°, and it is also attacked by carbonic anhydride at this temperature. Sulphur and phosphorus convert the iodide into sulphide and phosphide respectively, and boiling water gradually converts it into the blue oxide. Hydrochloric and hydrofluoric acids attack the iodide very slowly, but boiling nitric or sulphuric acid, or aqua regia, converts it into tungstic anhydride. Aqueous potash or fused potassium hydroxide, alkali carbonates, or mixtures of alkali carbonates and nitrates readily oxidise the iodide. C. H. B.

Alums of Titanium Sesquioxide. By AUGUSTO PICCINI (*Zeit. anorg. Chim.*, 1898, 17, 355—362).—*Cæsium titanium alum*,



is obtained by dissolving precipitated titanic acid in a slight excess of dilute sulphuric acid, adding the theoretical quantity of a cold solution of cæsium sulphate, and then subjecting the mixture to electrolysis, using as a diaphragm an ordinary porous cylinder; the solution at the negative pole quickly becomes violet and deposits crystals of the alum. It is purified in an atmosphere of carbonic anhydride by recrystallisation from water acidified with sulphuric acid, when it forms pentagonal, hemihedral, bright violet crystals belonging to the cubic system; it is very sparingly soluble in cold water, more so in hot water, and the solution quickly becomes turbid on exposure to the air, with precipitation of titanic acid. When heated in the air, it is oxidised, giving off vapours of water and sulphuric acid.

Rubidium titanium alum, $Ti_2(SO_4)_3.Rb_2SO_4 + 24H_2O$, prepared in a similar manner to the cæsium salt, crystallises in transparent, bright red crystals belonging to the cubic system; it is very similar to the cæsium salt, but is more soluble in water.

The author was unable to obtain the potassium or ammonium alum in a crystalline condition. He points out that cæsium sulphate is the best salt to employ for determining whether a sesquioxide is capable of forming alums, and mentions that cæsium manganese alum, $Me_2(SO_4)_3.Cs_2SO_4 + 24H_2O$, is easily obtained by the method described above. E. C. R.

Alkali Thioantimonites. By POUGET (*Compt. rend.*, 1898, 126, 1144—1145).—Sodium thioantimonite, Na_3SbS_3 , is obtained on dissolving antimony sulphide in sodium sulphide solution and evaporating in an atmosphere of hydrogen. It forms colourless needles which act strongly on polarised light, and have the composition $Na_3SbS_3 +$

$9\text{H}_2\text{O}$; they become anhydrous when heated above 150° in a current of hydrogen. The compound oxidises very readily in solution and yields the thioantimonate and a black compound, $2\text{Sb}_2\text{S}_3, 3\text{Na}_2\text{S}$.

Sodium pyrothioantimonite could not be obtained by the same method as the potassium salt, owing to the difficulty of preventing oxidation. If the solutions are concentrated by heat they yield thioantimonite and the insoluble black metathioantimonite, NaSbS_2 ; when dilute solutions are evaporated in a vacuum, they yield small red crystals of the compound $\text{Na}_2\text{Sb}_4\text{S}_7 + 2\text{H}_2\text{O}$, analogous to the potassium salt described by Ditte.

When precipitated antimony sulphide is mixed with a cold concentrated solution of ammonium sulphide, it is partly converted into the normal thioantimonite, which dissolves and can be precipitated as a white, crystalline powder by adding alcohol, and partly into crystals of the insoluble metathioantimonite, NH_4SbS_2 . In presence of air, or when heated, these crystals are converted into small red crystals of the compound $(\text{NH}_4)_2\text{Sb}_4\text{S}_7$, which is comparatively stable, and is the only product when the antimony sulphide is dissolved in a hot or a somewhat dilute solution of ammonium sulphide. C. H. B.

Aqueous Solutions of Metallic Gold. By RICHARD ZSIGMONDY (*Annalen*, 1898, 301, 29—54).—A red solution of metallic gold in water may be prepared by treating a feebly alkaline, boiling solution of gold chloride with a reducing agent; formaldehyde is the most suitable, less satisfactory results being obtained with acetaldehyde, alcohol, or hydroxylamine. The solution is not always red and clear; it is often dark-purple, violet, or bluish-black, and appears turbid, especially if the formaldehyde is not mixed rapidly with the gold solution. The presence of minute quantities of phosphates of the alkaline earths is sufficient to prevent the formation of these red solutions.

The metallic solutions prepared according to directions given in the paper are very dilute, 100 c.c. containing about 0.005 gram of gold; when boiled, they undergo no change until somewhat less than half the original volume in bulk, when they become violet-black, and deposit gold as a black powder. Dialysis affords the most satisfactory means of concentrating the solutions, which become of an intense red, and finally contain 0.12 per cent. of colloidal gold. Such solutions are tasteless. They become blue when treated with solutions of neutral salts, which slowly precipitate finely divided gold, leaving the liquid colourless; potassium ferrocyanide, however, develops a green coloration, which subsequently becomes yellow, without precipitation of the metal. Mineral acids produce the same effect as neutral salts, but acetic acid changes the red colour of the solution to violet-red, and finally black, gold being precipitated slowly; alkalis precipitate blue gold, whilst ammonia is without influence. Excess of alcohol gradually changes the colour of gold solutions to dark violet, completely precipitating the metal, which retains the property of dissolving in water (compare Schneider, *Abstr.*, 1892, 775). Aqueous solutions of metallic gold behave like most other dissolved colloids when submitted to the action of a current of electricity; the metal travels with negative electricity, but fails to penetrate the membrane. Mercury is

without action on gold dissolved in water. Solutions which have not been purified and concentrated by dialysis develop, during one or two weeks, small cultures of mould; these decolorise the solutions without precipitating the metal, which appears to be absorbed in the mycelium.

The absorption spectra of the gold solutions have been compared with those of gold glass and thin sheets of the metal. M. O. F.

NOTE.—In the collection of chemical specimens at Guy's Hospital is a solution of colloidal gold, prepared more than 30 years ago. There has been no perceptible change in the deep red colour during the last 15 years, although the specimen has been constantly exposed to diffused daylight.—EDITOR.

Mineralogical Chemistry.

Roumanite. By CONSTANTIN I. ISTRATI (*Bull. Soc. Sci. Bucarest*, 1898, 7, 272—273. Compare Abstr., 1897, ii, 502).—Roumanite is noted from two new localities in Roumania, namely, in the districts of Prahova and Bouzéou. The new material is clear yellow and perfectly transparent; it has a spangled appearance, like aventurine, due to numerous minute fractures. Sp. gr. 1·0536 at 25°. Refractive index for sodium light, 1·53774. At 325°, it blackens, without fusing. Analysis gave

C.	H.	S.	Ash.
79·98	10·47	0·918	0·130
79·80	10·78	0·876	0·096

This is purer than the darker varieties, and contains less carbon and ash. L. J. S.

Natural Gas in East Sussex. By CHARLES DAWSON (*Quart. Journ. Geol. Soc.*, 1898, 54, 564—571. Compare following abstract).—From a boring made for water at Heathfield railway station, in August, 1896, there is a large escape of gas under considerable pressure. The boring reaches to the Purbeck series, and passes through bands of bituminous shale and lignite. Analysis of the gas by S. A. Woodhead gave

O.	CO.	CH ₄ .	Higher hydrocarbons.	Total.
18·0	4·0	72·5	5·5	100·0

L. J. S.

Natural Gas at Heathfield Station, Sussex. By JOHN THEODORE HEWITT (*Quart. Journ. Geol. Soc.*, 1898, 54, 572—573).—Analysis of the gas from the Heathfield boring gave the following results, which are quite different from those mentioned in the preceding abstract.

CH ₄ .	H.	N.	Total.
91·9	7·2	0·9	100·0

Oxygen, carbonic anhydride, carbonic oxide, olefines, and hydro-carbon vapours were absent in the sample analysed.

Carbonaceous shale from a depth of 300 feet in the boring contained

C.	H.	N.	S.	O.	Ash.	Total.
9.43	1.83	0.68	1.27	[4.97]	81.82	100.00

The ash of this gave on analysis

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	SO ₃ .	P ₂ O ₅ .	Alkalis and loss.	Total.
59.72	24.40	7.03	2.14	0.96	2.54	Nil	[3.21]	100.00

L. J. S.

Artificial Production of Periclase by a New Method. By AUGUST B. DE SCHULTEN (*Bull. Soc. fran. Min.*, 1898, 21, 87—88).—By heating potassium hydroxide and magnesium hydroxide at 200°, brucite (MgO, H₂O) was obtained (Abstr., 1885, 1183), whilst at a red heat periclase (MgO) is formed in limpid, regular octahedra. Potassium hydroxide (200 grams) and magnesia (8—9 grams) are fused at a red heat, the mixture allowed to cool slowly, and the crystals washed with chlorine water and nitric acid. Analysis showed the presence of 99.92 per cent. MgO, and traces of iron. Sp. gr. 3.566.

L. J. S.

Constitution and Formation of Bauxite. By G. L. BOURGEREL (*Chem. Centr.*, 1898, 1, 406; from *Mont. Scient.*, 1897, [iv], 12, 21—22).—The bauxites of the South of France (Dept. Var) are of various colours, the red (I) and the white (II) being well-marked varieties. The red is used for the manufacture of aluminium, and the white for the preparation of aluminium sulphate; intermediate varieties are mixed with plastic clay for the manufacture of refractory bricks.

	Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ .	TiO ₂ .	V, Cr, &c.	H ₂ O.
I (red)....	62—50	24—28	1—7	0.10—4	traces	12—13
II (white).	74—65	0.25—3	12—18	varies	—	14

The bed of bauxites has a thickness of 50 m., and occurs in sedimentary limestones. To account for the formation of bauxite, the author assumes interaction between quicklime and hot, concentrated solutions of aluminium and iron chlorides.

L. J. S.

Composition of Spar from Knaresborough. By B. ARTHUR BURRELL (*Proc. Yorks. Geol. and Polyt. Soc.*, 1898, 13, 284—285).—Celestite (SrSO₄) has long been known at Knaresborough, and strontium has been detected in the waters (Trans., 1896, 536); the rocks of the neighbourhood would therefore be expected to contain small quantities of strontium. With a view to testing this, the following analysis was made of brown crystalline spar from Mother Shipton's Cave,

SiO ₂ .	P ₂ O ₅ .	SO ₃ .	CO ₂ .	CaO.	MgO.	SrO.	Mn ₂ O ₄ .	Fe ₂ O ₃ .	Alkalis.
0.037	0.005	2.331	42.170	55.038	0.190	0.128	0.019	0.006	trace

This corresponds with CaCO₃, 95.494; CaSO₄, 3.793; SrSO₄, 0.227 per cent.

L. J. S.

Compact Muscovite from Montrambert (Loire). By GEORGES FRIEDEL (*Bull. Soc. fran. Min.*, 1898, 21, 135—137).—The schists met with in the coal mine of Montrambert contain, in contact with

the knots of quartz, a compact, apparently amorphous mineral, yellowish-green in colour; small fragments are colourless and transparent; sp. gr. 2·783. Microscopical examination of thin sections shows that it consists of a confused, or sometimes plumose, aggregate of lamellæ and fibres having the optical characters of muscovite. Analysis gave

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
45·77	37·70	1·98	0·95	0·89	0·75	7·66	4·51	100·21

This agrees with the muscovite formula $RO, Al_2O_3, 2SiO_2$ where $R = \frac{2}{3}H_2 + \frac{1}{3}(K_2, Ca, \&c.)$. The mineral differs from alteration products of the pinite group in its transparency and mode of occurrence; and it is to be regarded as a peculiar variety of sericite. L. J. S.

Jadeitite from Piedmont. By L. MRAZEC (*Bull. Soc. Sci. Bucarest*, 1898, 7, 187—196).—The rock described is a rolled pebble of a fine dark green colour with white spots, and resembles jade in appearance, toughness, and fracture. Sp. gr. 3·346. Analysis of the green portion gave

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Loss on ignition.	Total.
56·92	trace	18·74	5·73	trace	4·31	2·64	12·11	trace	0·25	100·70
56·64	trace	18·33	6·41	trace	4·83	2·46	—	trace	—	—

This green portion has the optical characters of pyroxene, and it is therefore jadeite; the white spots are felspar, probably oligoclase. For this rock (jadeite-pyroxenite of Berwerth), the name jadeitite is proposed; it has a slightly schistose structure, and is supposed to be of dynamometamorphic origin (compare *Abstr.*, 1896, ii, 310—311; 1897, ii, 508). L. J. S.

Ferruginous Colouring Matters of Sedimentary Deposits and the Probable Origin of Red Rocks. By WALTHER SPRING (*Rec. Trav. Chim.*, 1898, 17, 202—221).—Ferruginous rocks can be divided into four groups, green, ochre-yellow, wine-red, and black. The author attempts to explain the presence of two or more of these in the same strata, for example, in the Devonian series. It is shown that the yellowish-brown rocks do not owe their colour merely to ferric hydroxide as previously supposed, but to a compound of ferric hydroxide with a colourless oxide such as silica, magnesia, lime, or alumina, and as these compounds are much more stable than ferric hydroxide, they retain their colour when dehydrated, only turning brick-red on calcination, and at the same time becoming magnetic; they also resist the action of saline waters better than the simple hydroxide. The green rocks do not owe their colour to a simple ferrous silicate, but to a ferroso-ferric silicate, they are thus a special group of the black rocks coloured by magnetite.

Ferric hydroxide, when in a compact form, retains its water only in an atmosphere the humidity of which is equal to its dissociation tension and at not too high a temperature; in a light form, under water, it crystallises and becomes dehydrated. J. J. S.

Meteoric Irons. By EMIL W. COHEN (*Ann. k.k. naturhist. Hofmus. Wien*, 1898, 13, 45—58).—*Smithland*, Livingston Co., Kentucky. Analysis I corresponds with the mineralogical composition: nickel-iron, 99.00; schreibersite and rhadbite, 0.58; troilite, 0.27; daubréelite, 0.15 = 100.00; sp. gr. 7.7115.

Botetourt, Virginia. This is an ataxite rich in nickel; analysis II (on 17 mg.). The sp. gr., 8.186, is higher than that of any other meteorite. Specimens in the Göttingen collection are shown to be artificial.

Scriba, Oswego Co., New York. The structure is that of artificial iron, and the composition (analysis III) is not against this, since small quantities of cobalt, up to half a per cent., have been found in artificial irons.

Hemalga, Tarapaca Desert, Chili. The cavities contain metallic lead and a black slag composed of iron, silica, and calcium. The deficiency in analyses IV and V represents oxygen in the slag and in lead oxide and carbonate. Although the structure resembles that of an ataxite, the physical characters and composition prove this iron to be a pseudometeorite.

Nauheim, Wetterau, Grand Duchy of Hesse. In structure and composition this is an artificial iron; besides 79.97 per cent. of metallic iron, it contains 18.10 per cent. of $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$.

St. Augustine's Bay, Madagascar. This is also shown to be an artificial iron containing no nickel.

Analyses I—V (and others) by O. Sjöström.

	Fe.	Ni.	Co.	P.	S.	Cr.	C.	Pb.	SiO ₂ .	Residue.	Total.
I.	82.83	16.42	0.94	0.09	0.17	0.06	—	—	—	—	100.51
II.	85.88	18.23		trace	—	—	—	—	—	—	104.11
III.	99.79	nil	0.27	0.09	—	—	0.06	—	—	—	100.21
IV.	81.89	nil	nil	not det.	—	—	—	9.12	1.26	1.17	93.44
V.	77.51	nil	nil	0.02	—	—	—	11.64	2.05	2.60	93.82

It has recently been stated that, while pyrrhotite is a conductor of electricity, troilite is a non-conductor. New experiments, however, show that troilite taken from several meteoric irons is a good conductor.

L. J. S.

Meteoric Iron from Cincinnati, U.S.A. By EMIL W. COHEN (*Sitz.-Ber. Akad. Berlin*, 1898, 428—429).—All that is known of the history of this iron is that it was presented to the Munich collection by Hosaeus. The etched surface is lumpy and pitted, but varies in character in different portions, and is in parts granular; it is suggested that this structure may be due to the presence of fine lamellæ of troilite. A little schreibersite is present. Analysis by O. Sjöström gave

Fe.	Ni.	Co.	Cu.	P.	S.	Cr.	Total.	Sp. gr.
94.47	5.43	0.68	0.01	0.05	0.05	nil	100.69	7.6895

This corresponds with 99.54 per cent. of nickel-iron. The structure resembles, but does not completely agree with, that of the Campo del Cielo and Siratik irons; and the three may be grouped together as ataxites poor in nickel.

L. J. S.

Chalybeate Waters in Silesia. By ERNST LUDWIG and V. LUDWIG (*Chem. Centr.*, 1898, 1, 1036; from *Wien. klin. Woch.*, 1898, 11, 207—210).—Analyses are given of waters from the “Marien” and “Paula” springs at Johannisbrunn. L. J. S.

Gases from the Abano Springs and the Boracic Soffioni of Tuscany and the Combustible Gas from the Bolognian Apennines. By RAFFAELE NASINI, FRANCESCO ANDERLINI, and ROBERTO SALVADORI (*Gazzetta*, 1898, 28, i, 81—153).—The authors have examined and analysed the gas escaping with hot mineral water at Monte Irone in Abano, the gas from the Casotto soffione and the Tini soffione at Larderello in Tuscany, and the combustible gas from the mineral water of the Porretta baths. The gas from the first source contains 72 per cent. of nitrogen, 12 of methane, 15 of carbonic anhydride, and a little hydrogen sulphide; that from the second and third consists principally of carbonic anhydride with a little hydrogen sulphide, whilst the Porretta gas contains about 90 per cent. of methane. The unabsorbed residues containing the nitrogen were in each case examined; that from the Abano gas contains 2 per cent. of argon with a little helium, whilst that from Larderello gas contains 2 per cent. of argon and 1 per cent. of helium, thus affording a good source of helium, which the authors propose to utilise. The residual gas from the Bolognian Apennines contains no helium and 2 per cent. of argon.

The results obtained from the spectroscopic examination, and drawings of the apparatus used, are given. W. J. P.

Physiological Chemistry.

Experiments with Sheep on the Digestibility of several kinds of Dried Distillery-residues. By OSCAR KELLNER, A. KÖHLER, F. BARNSTEIN, and L. HARTUNG (*Landw. Versuchs-Stat.*, 1898, 50, 297—316).—The residues investigated were derived from (1) maize and rye, with potatoes and some barley; (2) mainly oats and maize with some barley; (3) maize, barley, and oats; (4) rye, maize, oats, and some barley; (5) barley and maize, with rye and potatoes.

Two sheep were fed with a mixture of hay and each of the above residues in succession. It was found that the digestibility of the residues greatly varied, the difference being considerable even when the chemical composition was similar. The digestibility cannot be judged either from the nature of the products from which the residues are produced, or from the chemical composition. For the purpose of valuation, the amount and digestibility of the proteids should be ascertained.

The great variation in the digestibility coefficients of the proteids (49—79·5) depends chiefly on the temperature and time employed in drying the residues. Residues such as those which contain chaff, and are consequently readily dried, are more digestible, as regards proteids, than the more doughy ones. The fat was, in every case, nearly all

(92—94 per cent.) digested, and the non-nitrogenous extract was in some cases to a great extent digested. N. H. J. M.

Requirement of Food and Energy of Full-grown Fattened Bullocks. By OSCAR KELLNER and A. KÖHLER (*Landw. Versuchs-Stat.*, 1898, 50, 245—296).—The results of previous experiments indicated that the weight of fattened animals can be maintained with rations corresponding with maintenance feeding, but did not prove that the substitution of fattening rations by maintenance food does not result in a loss of flesh or fat. Loss of fat would be accompanied by gain in water. The experiments now described were made with three fat bullocks, and lasted 15 or 16 days. The fæces were examined every 12, the urine every 24 hours, whilst the respired gases (carbonic anhydride and methane) were determined 4 or 5 times during a period of exactly 24 hours.

As regards the amounts of food constituents necessary to maintain full-grown, fat bullocks in good condition, it is concluded that 0·85 kilo. of crude proteid, and 6·64 kilos. of non-nitrogenous food, per 1000 kilos. live weight, are sufficient. This includes 13 grams of proteid, and an amount of non-nitrogenous substance corresponding with 106 grams of fat, available for the continuous production of hair, hoofs, and skin, &c. Wolff's figures (digestible crude proteid, 0·75 kilo., and non-nitrogenous substance, 8·25 kilos.) may, therefore, be adhered to in practice, and it is only necessary to give the food in the form most readily consumed by the animals. The substance gained during fattening is not only not lost, but there is a slight further gain of fat. Any disturbance of the animals must be avoided, and the change of fattening to maintenance food must not be too sudden. Finally, the animals must always be kept in stalls with plenty of litter.

Deducting the heat values of the fæces, the urine, and the methane from that of the food, the average result for the three bullocks was found to be 24979 Cal., with a temperature of 15·7° in the stalls. Fattened animals would thus seem to require a slightly greater amount of energy supplied than lean animals, which may be accounted for on the supposition that a given amount of mechanical work requires greater exertion on the part of a fat than of a lean animal of equal muscular power. The difference is, however, only slight, and need not be taken into account in practice.

When food, both readily digestible and as palatable as possible, is given to cattle *ad lib.*, not only is the fattening period reduced, but less food is required than with smaller rations. N. H. J. M.

Sugar as a Food. By AUGUSTE CHAUVEAU (*Compt. rend.*, 1898, 126, 795—802).—The general conclusions arrived at in this paper are as follows. The quantities of sugar, or of fat, that it is necessary to add to a given ration of meat in order to obtain the best diet for a man in work are not isodynamic quantities. An energy value of 0·756 in sugar is generally as effective as an energy value of 1·0 in the form of fat, and under some conditions the advantage of sugar may be still greater. In the case of sugar, the ratio of nutritive value to energy value is not constant, but may increase con-

siderably when new tissues are being formed or an exhausted organism is being revived, whereas in the case of fat the ratio remains practically constant. The increase in the relative nutritive value of the sugar is due to the fact that it promotes assimilation of proteids and reduces dissimilation. It follows that if it is misleading to deduce the nutritive value of a food simply from its heat of combustion, it is equally wrong to deduce this value exclusively from the facility with which the food is converted into muscular glycogen. As a matter of fact, the nutritive value of a food depends, not only on the energy that it is capable of supplying, but also on the indirect influence that it is capable of exerting in the renewal and formation of the anatomical elements of the body. From whatever point of view the matter is regarded, however, the superiority of sugar over fat is very distinct.

The author has reason to believe that these conclusions apply in the case of men at rest as well as in the case of men at work.

C. H. B.

Sulphuric Acid in Bone Ash. By P. BIELFELD (*Zeit. physiol. Chem.*, 1898, 25, 350—354).—Mörner attributes the sulphuric acid found in bone ash, not to collagen, but to chondroitin-sulphuric acid. The high percentage given by some observers is due to the use of coal gas in the process of incineration. This last fact is confirmed in the present research, which is devoted to the examination of the question in fetal bones. The quantity of sulphuric acid in ox bone is 0.04, in calf embryos 0.06 per cent.

W. D. H.

The Antecedents of Urea. By JOHN T. HALSEY (*Zeit. physiol. Chem.*, 1898, 25, 325—336).—Hofmeister (*Arch. exp. Path. Pharm.*, 37, 426) showed that, by the oxidation of numerous organic substances, both nitrogenous and non-nitrogenous, by means of potassium permanganate in the presence of excess of ammonia, urea was formed. Among the substances employed were derivatives of methane, amido-acids, proteids, hydroxy-acids of the fatty series, glycol, pyrogallol, acetone, and oxamic acid. Ethylic alcohol, acids of the acetic and oxalic series and their amides (except formamide), acetonitrile, formaldehyde, dextrose, and a number of other substances yield no urea under these conditions.

In the present research, it is shown that, in the cases where urea is formed, formamide and oxamic acid are intermediate stages in the process; there are probably other substances as well. Experiments on dogs lead to the conclusion that these substances are rapidly transformed into urea.

W. D. H.

Partial Decomposition of Chloroform in the Animal Organism. By ALEXANDRE DESGREZ and MAURICE NICLOUX (*Compt. rend.*, 1898, 126, 758—760).—Experiments with dogs show that, although the gas obtained from normal blood contains carbonic oxide to the extent of about 1.6 c.c. per litre of blood, the proportion of this gas is very markedly increased when anæsthesia is produced by means of chloroform, and may amount to as much as 6.9 c.c. when the anæsthesia is intense and prolonged. The proportion of carbonic oxide increases with the duration of the anæsthesia, other conditions being equal.

On the other hand, when ether is the anæsthetic, there is a reduction instead of an increase in the quantity of combustible gases obtained from the blood.
C. H. B.

Theory of Acid Poisoning. By HEINRICH WINTERBERG (*Zeit. physiol. Chem.*, 1898, **25**, 202—235).—Salkowski concluded from his own experiments (*Virchow's Archiv.*, 1873, **58**, 134) and from those of Gaetgens (*Centr. med. Wiss.*, 1872, No. 53) that there was a difference in the chemical organisation of herbivorous and carnivorous animals, because the latter are more immune to mineral acids than the former; this he attributes to the capacity the carnivora have of excreting an increased amount of fixed alkali to neutralise the acid. Later observers (Walter, *Arch. exper. Path. Pharm.*, 1877, **7**, 148; Hallervorden, *ibid.*, 1879, **10**, 125) are inclined to attribute this difference to the amount of ammonia rather than fixed alkali. The present research shows that there is no real difference between the two classes of animals, herbivora also having the power of secreting an increased quantity of ammonia to neutralise the excess of acid; there is, however, a quantitative difference between the two classes, in favour of the carnivora.

The amount of ammonia excreted is, within narrow limits, independent of the reaction of the food given, but depends on the amount of ammonium salts not converted into urea.

The diminution of the carbonic anhydride in the blood is the sum of the absolute and relative amounts of alkali, there being a direct relation between the amount of carbonic anhydride and the alkalinity of the blood.
W. D. H.

New Method of Disinfection. II. By REINHOLD WALTHER and ARTHUR SCHLOSSMAN (*J. pr. Chem.*, 1898, **57**, 512—534. Compare this vol., ii, 349).—A detailed description of the method already described (*loc. cit.*) is here given, including an account and sketch of Luigner's apparatus for dispersing the "glycoformal."

The authors discuss at some length the demands that are, and ought to be, placed on a disinfectant, and conclude by stating that although the above is not a perfect means of disinfecting, yet it approaches the ideal more nearly than any other known method.
A. W. C.

Chemistry of Vegetable Physiology and Agriculture.

Assimilation of Nitrogen by Phanerogamous Plants from Amines, Substituted Ammonium Salts, and Alkaloids. By L. LUTZ (*Compt. rend.*, 1898, 126, 1227—1229).—Experiments made under conditions precluding the action of micro-organisms show that phanerogams can obtain their nitrogen from amines of low molecular weight, such as methylamine and ethylamine, whereas benzylamine, pyridine, and betaine are incapable of assimilation. Substituted ammonium salts and alkaloids are also useless, whilst phenolic amines

are powerfully toxic. When placed in a medium containing nitrogen in a form incapable of being utilised, the plants were found to lose, in the gaseous state, a considerable part of the nitrogen which they originally contained.

N. L.

Examination of some cheap black Chinese Teas. By J. ZOLCINSKI (*Zeit. anal. Chem.*, 1898, 37, 365—374).—The author has estimated moisture, caffeine, total nitrogen, total soluble matter, and ash in a number of cheap teas, and also determined the sp. gr. of an extract made with 10 parts of boiling water. Comparing his results with those of König, Weyrich, Geissler, and Bell, he concludes that the samples were all genuine and of good quality. The average amount of caffeine found was 1·55 per cent., and the average sp. gr. of the extract 1·0088 at 15°.

M. J. S.

Composition of Polenta made from Sound and Unsound Maize Flour. By DEODATO TIVOLI (*Gazzetta*, 1898, 28, i, 64—78).—The prevalence of pellagra in Italy has been attributed to the eating of polenta made with unsound maize flour. The author has, therefore, examined polenta made from the sound and unsound flour in order to ascertain whether marked differences in composition exist; the water lost at 100°, the acidity, the total nitrogen, the nitrogen in the soluble and insoluble constituents, the percentage extracted by ether and by water, the reducing power, the ash, the ash from the aqueous solution, the sodium chloride, and the cellulose were all determined.

Sound polenta contains rather less albuminoid nitrogen, and is much less acid in reaction than unsound; less ethereal extract or fatty matter is obtained from unsound polenta, and the power of reducing Fehling's solution is greater in the unsound polenta. The unsound polenta yields less ash, and contains much less sodium chloride, more matter soluble in water, and slightly less cellulose than sound polenta.

W. J. P.

Some Soils rich in Potash. By ARTHUR BORNTÄGER and G. PARIS (*Landw. Versuchs-Stat.*, 1898, 50, 343—345).—Soils of volcanic origin are rich in potash a part of which is soluble in water. Casoria found considerable amounts of potash in waters near Vesuvius (*Ann. R. Scuola. Sup. Portici.*, 1885, 5, part i).

The following analyses are given of four volcanic soils from the neighbourhood of Vesuvius. The mineral matter was extracted with boiling hydrochloric acid (sp. gr. = 1·12).

	Humus.	Nitrogen.	K ₂ O.	CaO.	P ₂ O ₅ .	Insoluble.
1.	—	0·0252	4·234	—	0·417	66·38
2.	—	0·3934	4·379	—	0·303	65·53
3.	—	1·00	5·050	—	0·684	64·80
4.	2·86	0·33	2·710	8·11	0·350	—

The soils contained only small quantities or traces of carbonates and sulphates, not much magnesia, but a good deal of lime and iron. Nos. 1 and 3 contained a little humus, No. 2 more.

N. H. J. M.

Effect of Crops and Manures on the Nitrogen Content of the Soil. By CHR. FR. A. TUXEN (*Landw. Versuchs-Stat.*, 1898, 50, 334—342).—Field experiments on rotation, permanent barley and permanent meadow have been made since 1863 at the Copenhagen Agricultural High School. The experiments included in each case an unmanured plot, and plots which received stable manure (18,000 kilos. until 1872, and 36,000 kilos. since) and artificial manures (nitrogen, 40·2; soluble phosphoric acid, 40; and potash 97 kilos. per hectare) respectively. Soil samples were taken, in 1886 and again in 1894, to the depth of 10 cm. and 10—20 cm., the method adopted being that employed at Rothamsted. Five samples were taken on each plot. The following summary shows the amount of nitrogen to the depth of 20 cm. in kilograms per hectare (1 kilogram per hectare = 0·89 lb. per acre).

	Meadow.		Barley.		Rotation.	
	1886.	1894.	1886.	1894.	1886.	1894.
Unmanured	4931	4638	3578	3470	4407	5025
Artificial manures	5131	5010	3639	3403	4582	5185
Stable manure	5842	6793	4596	4804	4593	6164

The soil is loamy, with a loam subsoil.

The yield of hay diminished after some time, increased in 1884, but since 1886 the yield was inconsiderable; this is owing chiefly to unfavourable climatic conditions. Barley and the rotation crops have, however, not fallen off to any extent.

As regards the amount of nitrogen in the soil, the herbage of the permanent meadow had the most favourable effect, due partly to the leguminous plants, and partly to the retention of nitrogen compounds supplied by the rain, which amounts in Denmark to 15 kilos. of nitrogen per hectare per annum. Moreover, in the case of meadow land, which remains cooler and drier in the summer than land more or less bare, nitrification is more or less diminished, whilst the comparatively small amount of nitrate formed is at once assimilated without loss.

The rotation land, whether manured or not, contained about 900 kilos. of nitrogen more than the barley land after 22 years, and very much more after 30 years.

Comparing artificial nitrogenous manure (in this case ammonium sulphate) with farmyard manure, the results show that only the latter enriches the soil to any extent.

N. H. J. M.

Analytical Chemistry.

Graduated Apparatus. By A. HÉMOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 343—344).—Flasks and pipettes are marked with a scale of temperatures, so as to allow of the measurement, at any temperature between 4° and 30° , of a quantity of water which shall occupy a standard volume at 4° .
N. L.

Caution against Alkali Glass. By CARL T. LIEBERMANN ((*Ber.*, 1898, 31, 1818).—Attention is drawn to the large proportion of soluble alkali occurring in certain sorts of alkali glass. M. O. F.

Determination of the Specific Gravity of Small Quantities of Gas. By TH. SCHLÖSING, jun. (*Compt. rend.*, 1898, 126, 896—899).—The author has applied his apparatus (this vol., ii, 324, 325), as a manometer, to the determination of the solubility of carbonic anhydride in sulphuric acid with the following results.

100 c.c. of acid of sp. gr. 1.845 dissolve, at 11.3° , 111 c.c. and at 30.2° , 77 c.c. of carbonic anhydride.

100 c.c. of acid of sp. gr. 1.733 dissolve, at 10.7° , 43 c.c. and at 30.2° , 27 c.c. of carbonic anhydride.

In order to make the apparatus applicable to all kinds of gases, the tube containing the gas to be examined is divided into three parts, horizontal serpentines of glass tube being inserted between the first and second and the second and third. In making an experiment, the lowest section of the tube is filled with carbonic anhydride, and the middle section with the gas under examination, whilst the upper section, as well as the second tube of the apparatus, remain filled with air. Under these conditions, any interdiffusion of the gas experimented on with either the carbonic anhydride or the air takes place in the serpentines, and, since these are horizontal, does not affect the level of the gaseous columns. Moreover, the gas under examination, which occupies the middle section of the tube, always has the same vertical length, which can be measured once for all. Determinations of the sp. gr. of nitrogen, carbonic anhydride, and sulphurous anhydride made with this apparatus agree with those made by older methods.
C. H. B.

Apparatus for the Extraction of large Volumes of Liquid with Ether. By HANS MALFATTI (*Zeit. anal. Chem.*, 1898, 37, 374—377).—The ether is boiled in a flask, and the condensed vapour falls into a kind of thistle-headed funnel, with a tube about a metre long inserted concentrically into a wider tube, through which the liquid to be extracted flows downwards in a continuous stream, being admitted by a side tube a little way below the top, and escaping at the bottom through an upturned tube rising about half the height of the column. The ether rises through the column of descending liquid, and overflows into the flask by a side tube inserted above the inlet for the other liquid. The contact of the two is prolonged by winding

wool, or other suitable material, spirally round the inner tube. A drawing of the apparatus accompanies the paper. M. J. S.

Inaccuracies in the Estimation of Carbon and Hydrogen by Combustion. By CHARLES F. MABERY (*J. Amer. Chem. Soc.*, 1898, 20, 510—513).—The author has proved by a number of combustions of petroleum that the ordinary form of potash-bulb loses moisture, an additional sulphuric acid tube still showing an increase in weight amounting to 1—2 milligrams. Another difficulty experienced was the presence of carbonaceous impurities in the granular copper oxide. If this is heated for several hours in pure oxygen, it is obtained quite free from impurities. L. DE K.

The Error in Estimations of Carbon where Weighed Potash-bulbs are Employed. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1898, 20, 528—534).—The author again confirms the statement that it is very difficult to obtain good results with carbon estimations in damp weather.

Blair's proposal to correct the error by placing an empty potash-bulb on the opposite pan, which might be supposed to condense the same amount of moisture on its surface, has been found to be illusory. The tabulated results show that it is impossible to get anything like true blanks in very damp weather.

The true remedy will, no doubt, be found in the use of smaller potash-bulbs or the substitution of soda-lime tubes. L. DE K.

Absorption of Oxygen by Potassium Pyrogallol. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 126, 1066—1072).—The author has made experiments with a view to ascertain under what conditions alkaline pyrogallol will absorb oxygen without liberating carbonic oxide.

A solution of 32 grams of pyrogallol in 100 c.c. of water, mixed with rather more than three equivalents of potassium hydroxide, will absorb ninety-two times its volume of oxygen, the absorption being at first rapid and afterwards slow. The volume of carbonic oxide liberated is about one seventy-fifth of the oxygen absorbed. The results are the same whether the oxygen is added all at once or in successive small portions, and are not appreciably affected by difference of temperature between 15° and 62°. Variations in the concentration of the alkali solution between somewhat wide limits affect neither the final result nor the relative velocity of the reaction; moreover, it is practically the same whether the pyrogallol is mixed with one equivalent of potassium hydroxide or with three, but if only half an equivalent of the hydroxide is added, the absorption of oxygen is also reduced to one-half, whilst the proportion of carbonic oxide liberated increases.

The proportion of carbonic oxide liberated is reduced to a minimum when the pyrogallol is mixed with a considerable excess of alkali, and when the quantity used is sufficient to absorb four or five times as much oxygen as it is placed in contact with.

When the reaction reaches its limit, three atoms of oxygen are absorbed for each molecule of pyrogallol present. C. H. B.

NOTE BY ABTRACTOR.—The fact that no carbonic oxide is liberated when potassium hydroxide is present in considerable excess has previously been observed by Clowes (*Proc.*, 1895, 200).

Determination of Sulphur in Illuminating Gas. By ANTONIO LONGI (*Gazzetta*, 1898, 28, i, 1—11).—The author has devised a modification of the apparatus used by Drehschmidt for the determination of sulphur in coal gas; the new apparatus, which is described in detail, is constructed wholly of glass, so as to avoid danger of the sulphuric acid produced attacking the metal in the lamp chimney, and is comparatively inexpensive. The lamp burns 10—15 litres of gas per hour, and the products of combustion are drawn by a water pump through two absorption cylinders filled with glass beads moistened with a solution of bromine in potassium carbonate; after the combustion has been effected, the sulphuric acid is estimated as barium sulphate in the liquor rinsed from the beads. The air serving for the combustion is purified by passing it through a tower containing pumice saturated with potassium carbonate and potassium permanganate.

Test analyses, made by burning hydrogen previously passed over weighed quantities of heated silver sulphide or silver thiocyanate, show the method to be accurate.

W. J. P.

Apparatus for the Estimation of Free Nitrogen in Purified Coal-gas. By GEORGES ARTH (*Bull. Soc. Chim.*, 1897, [iii], 17, 427—432).—The gas under examination is contained in a glass holder, where it is measured at a known temperature and pressure, and from which it is expelled by water. It is then passed through concentrated sulphuric acid to remove nitrogenous basic compounds, and burnt in an ordinary combustion tube charged with cupric oxide, the nitrogen being collected and measured as in Dumas' process. A current of carbonic anhydride is passed through the apparatus before and after the operation. A sketch of the apparatus is given.

N. L.

Reactions of Carbonic Oxide. By ARMAND GAUTIER (*Compt. rend.*, 1898, 126, 871—875).—Absorption with cuprous chloride is inapplicable to the determination of minute quantities of carbonic oxide, owing to the interference of acetylene and other hydrocarbons. Ammoniacal silver nitrate is also of comparatively little value, because the reaction varies with the concentration of the solution and its temperature; the oxidation is frequently incomplete, and the silver nitrate is reduced by gases other than carbonic oxide.

Oxidation of the carbonic oxide by potassium permanganate in presence of silver salts, as recommended by Mermet, is open to the objection that many other gases act on the reagent in a similar manner.

Chromic acid in concentrated aqueous solution oxidises carbonic oxide incompletely, even in presence of sulphuric acid. Potassium permanganate solution, 1 gram per litre, oxidises carbonic oxide very slowly, but a solution of 10 grams per litre acts very much more rapidly, even in the cold, carbonic anhydride and non-volatile acids being formed.

A solution of iodic acid containing 10 grams per litre has no action on the gas in the cold, but with a solution of 100 grams per litre at 100° there is a distinct reaction, with liberation of iodine and produc-

tion of carbonic anhydride. The reaction with iodic anhydride recommended by Ditte (compare Nicloux, below) is quantitative, begins at 40° , or even below, and is rapid and complete at 60° .

Gold chloride solution (1 in 100) is an excellent reagent for carbonic oxide, the reaction being almost instantaneous even in the cold, whilst the purple reduced gold settles rapidly. It is essential that the air tested with this reagent should be free from dust and contain no other reducing gases.

Moist silver oxide slowly absorbs carbonic oxide with formation of silver subcarbonate, Ag_4CO_3 , which is only slowly attacked by dilute acetic acid, but is completely decomposed by dilute sulphuric acid with liberation of carbonic anhydride, the other products being silver sulphate, metallic silver, and water. Traces of formic and oxalic acids are formed at the same time as the subcarbonate.

Mercuric and mercurous oxides seem to have no action on carbonic oxide.
C. H. B.

Detection of Carbonic Oxide by means of Palladium Chloride. By POTAIN and RENÉ DROUIN (*Compt. rend.*, 1898, 126, 938—940).—A solution of palladium chloride, 1 part in 10,000, may be used as a reagent for carbonic oxide, the air containing the gas being allowed to bubble in a very thin stream through 10 c.c. of the solution. If 10 litres of air are used, 1 part of carbonic oxide in 10,000 can be detected by the reduction of the chloride to metallic palladium, but the method does not lend itself to quantitative estimation.

Direct experiment shows that when mixtures of carbonic oxide with a large proportion of air are exposed to light, the carbonic oxide is gradually oxidised to carbonic anhydride, but the change is retarded and limited by the presence of carbonic anhydride. This observation probably explains why the proportion of carbonic oxide in the air of towns does not increase.
C. H. B.

Estimation of Minute Quantities of Carbonic Oxide in Air. By MAURICE NICLOUX (*Compt. rend.*, 1898, 126, 746—749).—The method proposed depends on the fact that, at 150° , carbonic oxide decomposes iodic anhydride, with liberation of iodine and formation of carbonic anhydride. The air to be examined is passed successively over potassium hydroxide and pumice moistened with sulphuric acid, and then through a U-tube containing iodic anhydride, and placed in an oil bath, this tube being connected with a Will's apparatus containing pure sodium hydroxide solution of sp. gr. 1.3 diluted with an equal volume of water. The air is aspirated through the tubes at the rate of about 10 c.c. per minute, and when the operation is completed the alkali solution is acidified with sulphuric acid, mixed with sodium nitrate, and agitated with 5 c.c. of chloroform, or, better, carbon bisulphide, the intensity of the rose tint being compared with that produced by known quantities of potassium iodide, $3\text{CO} = \text{KI}$. Air alone, hydrogen, and methane give no similar result, and the method is applicable to proportions of carbonic oxide varying from 1 in 1,000 to 1 in 50,000.
C. H. B.

Estimation of Small Quantities of Carbonic Oxide in Air. By ARMAND GAUTIER (*Compt. rend.*, 1898, 126, 793—795).—The reaction described by Nicloux (preceding abstract) has been employed in the author's laboratory for the estimation of small quantities of carbonic oxide during the last seven or eight years. It is applicable even when the gas is diluted with 20,000 vols. of air, and the reaction with the iodic anhydride proceeds regularly and completely at 60°, and also takes place at 40°, although slowly. At 60°, most hydrocarbons, with the exception of acetylene, have no action on the anhydride. The liberated iodine may be absorbed by copper and weighed, but the best plan is to estimate the carbonic anhydride by Muntz's method.

At temperatures higher than 60°, and especially at 150°, several hydrocarbons reduce iodic anhydride. Ethylene, although it does not directly attack the anhydride, has the peculiar property, even when present in small quantity, of preventing the oxidation of the carbonic oxide.

The *complete* liberation of iodine by nitrous acid takes place only under certain conditions. C. H. B.

Estimation of Carbonic Oxide in Air. By ARMAND GAUTIER (*Compt. rend.*, 1898, 126, 931—937).—The oxidation of carbonic oxide by iodic anhydride begins at 30°, is rapid at 40° to 45°, and is complete at 60—65°, no matter how large a proportion of air or nitrogen the oxide may be diluted with. The volume of carbonic anhydride formed is always equal to that of the carbonic oxide taking part in the reaction, and it is best estimated by the volumetric method of Muntz and Aubin (*Abstr.*, 1887, 468). Experiments with air containing known proportions of carbonic oxide show that the method is applicable when the proportion of the latter is so low as 1 part in 30,000, or even 1 part in 300,000.

Acetylene is oxidised by iodic anhydride, the reaction beginning at 35° even in presence of a large proportion of air. Ethylene is oxidised by iodic anhydride at 65°, and the presence of this gas interferes with the oxidation of carbonic oxide.

Methane and its homologues are not oxidised by the anhydride at 65—80°. C. H. B.

Estimation of Carbonic Oxide in Air and in Normal Blood. By LOUIS DE SAINT-MARTIN (*Compt. rend.*, 1898, 126, 1036—1039).—In the author's method of estimating carbonic oxide (*Abstr.*, 1892, 1128), the gas extracted from the cuprous chloride solution is measured before explosion, after explosion, and after treatment with potash; and from these data the composition of the gas can be calculated. There is, therefore, no risk of hydrocarbons being estimated as carbonic oxide, as Gautier supposes (compare preceding abstracts).

The author confirms the statement of Degrez and Nicloux (this vol., ii, 529) that carbonic oxide exists in small quantity in the normal blood of animals living in towns, but the quantity is less than 1 c.c. per litre. Great care is necessary to prevent confusion between carbonic oxide and hydrocarbons, and the author is unable to accept the statement of Degrez and Nicloux that the proportion of carbonic oxide in the blood is largely increased by the inhalation of chloroform.

C. H. B.

New Solvent for Distinguishing the Phosphoric Acid in various Phosphates. By WILHELM HOFFMEISTER (*Landw. Versuchs-Stat.*, 1898, 50, 363—369).—Whilst Wagner and Maercker have shown that the phosphoric acid of bone meal is not to be compared in value with that of basic slag, and Wagner's citric acid solution extracts far more phosphoric acid from the latter than from the former when the action is continued for half an hour, a greater amount of phosphoric acid (to 99 per cent.) is obtained from bone meal when the action of the citric acid is prolonged to 5—6 days than from basic slag (to 90 per cent.).

The following method gives results more in accordance with the ascertained manurial value of the two products. Humic acid (15 grams) dissolved in dilute ammonia is poured into a 2-litre flask containing some sand; the manure (5 grams) and at least 1 litre of water are then added, the whole shaken, and a moderately strong current of carbonic anhydride passed through for 12 days; ammonia should be added frequently. The liquid is then poured off, the sand washed, and the combined liquids, made up to a definite volume, are filtered, and four-fifths of the filtrate evaporated to dryness, after addition of hydrochloric acid. The residue is treated with water containing a little hydrochloric acid, filtered, washed, and the filtrate made up to 100 c.c. Portions of this are employed for estimating phosphoric acid, iron, and lime.

Basic slag containing 16.7 per cent. citrate soluble phosphoric acid gave 10.43 and 10.38 per cent. soluble in humic acid. In bone meal, and fermented bone meal, 1.01 and 1.48 per cent. of phosphoric acid dissolved in humic acid. When, however, the basic slag is first rubbed with alcohol, results almost identical with Wagner's are obtained; P_2O_5 (citrate soluble) = 18.53; soluble in humic acid, 18.48 and 18.45 per cent.

The method is too complicated to supersede Wagner's for basic slag, but is intended to distinguish between different phosphates. Fine bone meal, in which the phosphoric acid almost entirely dissolves in citrate solution, only yielded 1 per cent. with humic acid. The results show the great importance of manufacturers supplying basic slag in the finest possible form.

Humic acid dissolved the following percentages of the total phosphoric acid of different manures. Basic slag (fine), 95.8; Redonda phosphate, 30.38; bone precipitate, 43.3 per cent.

The humic acid is prepared from wood-lignin by extraction with ammonia vapour.

N. H. J. M.

Estimation of Potassium without previously Removing the Iron, Calcium, &c. By CHARLES C. MOORE (*J. Amer. Chem. Soc.*, 1898, 20, 340—343).—The solution, which must be free from ammoniacal salts, but may contain iron or aluminium chlorides and alkali sulphates, is mixed with sufficient platinum tetrachloride to insure the precipitation of the potassium, and the whole evaporated to a syrupy consistency; the residue is then treated with acidified alcohol, which dissolves the excess of platinum tetrachloride, and also the ferric and aluminium chlorides. When these compounds have been completely

removed, the sodium sulphates and chlorides are washed out with a 20 per cent. solution of ammonium chloride, and after this has been removed by means of 85 per cent. alcohol, the potassium platinochloride is dried and weighed as usual.

The acidified alcohol is prepared by passing dry hydrogen chloride into cold 90 per cent. alcohol until 1 c.c. neutralises 2.3 c.c. of normal alkali.

L. DE K.

Estimation of Lead in Alloys. By W. E. GARRIGUES (*J. Amer. Chem. Soc.*, 1898, 20, 508—510).—The process is based on the fact, noticed by the author, that lead chromate is not affected by ammonia, whereas copper chromate is readily soluble in it.

The nitric acid solution containing the lead and the copper is mixed with an excess of potassium dichromate, followed by ammonia in excess. After heating until the liquid clears, the lead chromate is collected on a Gooch crucible, and after being washed, first with dilute ammonia, then with hot water, and finally with alcohol, is dried in the water oven and weighed.

The author also communicates a process which admits of the estimation of the lead as sulphate, without previously removing any tin which may be present. About 0.5 gram of solder, for instance, is oxidised with nitric acid, 20 c.c. of sulphuric acid is added, and the solution is evaporated until dense sulphuric fumes appear. Eighty c.c. of water is then added, and after a few minutes the lead sulphate is collected on a Gooch crucible. The filtrate contains the tin in solution, which may be precipitated as hydrated oxide, by adding ammonia until it is alkaline, and then sulphuric acid until the liquid is faintly acid.

L. DE K.

Note on Drown's Method of Estimating Silicon in Steel. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1898, 20, 547—549).—The author has slightly modified Drown's process; 4.6667 grams of the sample of steel is treated in a beaker with 50 c.c. of a mixture of 500 c.c. of dilute nitric acid (2 : 3), 300 c.c. of sulphuric acid, and 200 c.c. of water. When the steel has dissolved, 15 c.c. of strong hydrochloric acid is added, a watch-glass is suspended over the beaker by three small, bent glass rods, and the liquid boiled down rapidly over a very hot iron plate, until fumes of sulphuric acid begin to appear. By this simple modification, the silicic acid is completely dehydrated, which is not the case if no hydrochloric acid is used.

L. DE K.

Analytical Notes on the Estimation of Phosphorus in Steel. By R. W. MAHON (*J. Amer. Chem. Soc.*, 1898, 20, 429—453). This is a very elaborate article on the vexed question as to what should be considered the best way of proceeding when testing steel for phosphorus by the molybdate method. It is again proved that long standing is of no advantage when Fresenius's molybdate solution is used for estimating phosphoric acid: the precipitation is complete within 10 minutes. It appears also, from a large number of experiments, that too much stress cannot be laid on the necessity of adding the magnesia mixture slowly. Other interesting details are given.

L. DE K.

Use of Hydrofluoric Acid in the Estimation of Manganese in Iron and its Ores. By ALLEN P. FORD and I. M. BREGOWSKY (*J. Amer. Chem. Soc.*, 1898, 20, 504—506).—The process based on the conversion of the manganese into manganese dioxide by treating samples of iron with nitric acid and potassium chlorate has this disadvantage, that much silicic acid is also precipitated, and causes inconvenience by clogging the filter. The authors now recommend adding a few drops of hydrofluoric acid, which instantly dissolves the silica; the use of this acid renders the beakers somewhat unsightly, but does not prevent them from being used a long time for the same kind of work.

In testing ores by the chlorate method, it has always been noticed that the precipitation of the manganese is never complete in one operation, but that the filtrate must always be tested again. The authors now state that when hydrofluoric acid is used, the precipitation is at once complete.

L. DE K.

Antimonic Tungstates: Separation of Tungsten and Antimony. By L. A. HALLOPEAU (*Bull. Soc. Chim.*, 1897, [iii], 17, 170—175. Compare Abstr., 1897, ii, 178).—To estimate antimony in antimoniotungstates, the solution is mixed with mercurous nitrate and the precipitate of mercurous antimoniotungstate collected, washed, and ignited. The mixture of tungstic acid and antimony tetroxide thus obtained is fused with a large excess of potassium cyanide, when the antimony is reduced to the metallic state, and is eventually washed with water and dilute alcohol, dried at 100°, and weighed. N. L.

Applications of Hydrogen Peroxide to Quantitative Analysis. By PERCY H. WALKER (*J. Amer. Chem. Soc.*, 1898, 20, 513—515).—*Separation of Titanium from Iron.*—The solution, which should measure about 150 c.c. and contain about 0.2 gram of the mixed metals, is mixed with 100 c.c. of a 2.5 per cent. solution of hydrogen peroxide and run in from a dropping funnel into a large beaker containing 100 c.c. of hydrogen peroxide and 30 c.c. of strong ammonia. The iron precipitate is washed with dilute ammonia to which some hydrogen peroxide has been added, but, as it still retains a considerable amount of titanium, it should be dissolved in a little hydrochloric acid and again treated with ammoniacal hydrogen peroxide; it is advisable to treat it in this way a third time. The mixed filtrates are boiled to precipitate the titanium as hydroxide, which is then washed with hot solution of ammonium nitrate and converted into oxide by ignition.

Separation of Uranium from Iron.—The slightly acid solution containing about 0.2 gram of the mixed metals is treated with 50 c.c. of hydrogen peroxide, and run slowly into a solution of 5 grams of sodium hydroxide in 50 c.c. of water containing 50 c.c. of hydrogen peroxide; the whole is then diluted with hot water to about 400 c.c. and filtered. The filtrate, which contains all the uranium, is acidified with hydrochloric acid and evaporated to dryness at 110°, and the uranium finally precipitated from the hydrochloric acid solution by ammonia and weighed as oxide.

Separation of Zirconium from Uranium.—About 0.3 gram of the

mixed metals is fused with 7 grams of sodium pyrosulphate, the melt dissolved in cold water, and the solution, mixed with 50 c.c. of hydrogen peroxide, is poured into a mixture of sodium hydroxide and hydrogen peroxide; on heating for half an hour on the water bath, the zirconium is gradually precipitated. After washing it with hot water, it is dissolved in a mixture of hydrochloric acid and hydrogen peroxide, boiled, and then precipitated with ammonia. The zirconium is finally weighed as oxide.

L. DE K.

Colorimetric Estimation of Small Amounts of Chromium in Rocks and Ores. By WILLIAM F. HILLEBRAND (*J. Amer. Chem. Soc.*, 1898, 20, 454—460).—The author has invented a very accurate process for the estimation of chromium in minerals when it only occurs in small quantity; 5 grams of the mineral, which often contains vanadium as well as chromium, is fused in a platinum crucible with 20 grams of sodium carbonate and 3 grams of sodium nitrate, avoiding too high a temperature. The melt is treated with hot water and a few drops of alcohol to reduce any manganese, and the solution filtered and nearly neutralised with nitric acid. On heating, the bulk of the silica and alumina separates; but, as this may retain some chromium, it should be treated with hydrofluoric and sulphuric acid to remove the silica, and the residual alumina must then be again fused with the oxidising mixture. To the mixed filtrates, mercurous nitrate is added, and the precipitate, after being ignited, is fused with a little soda; the melt is then dissolved in water, filtered, and diluted to 50 or 100 c.c. The yellow liquid is now introduced into a special colorimetric apparatus devised by the author, but ordinary Nessler tubes also answer the purpose. For comparison, a solution is used containing 0.25525 (or double) gram of pure potassium chromate in one litre of water rendered alkaline with sodium carbonate; each c.c. of the solution represents 0.1 milligram of chromic oxide.

If the amount of chromium exceeds 0.2 per cent., the treatment with nitric acid and mercurous nitrate may be omitted.

L. DE K.

Volumetric Estimation of Vanadium in Presence of Small Amounts of Chromium, with Special Reference to the Analysis of Rocks and Ores. By WILLIAM F. HILLEBRAND (*J. Amer. Chem. Soc.*, 1898, 20, 461—467).—The precipitate produced by mercurous nitrate (preceding abstract) also contains any vanadium present, which passes into the alkaline solution along with the chromium. The amount of chromium is first estimated colorimetrically, and it is then reduced to the chromic state by adding sulphuric acid and sulphurous acid, which also reduces the vanadium. After boiling off the excess of sulphurous acid and cooling to 80°, the vanadium may be titrated with standard permanganate. As, however, at that temperature, the chromic oxide also reduces the permanganate, a check must be made on a liquid containing exactly the same amount of reduced chromate, and the number of c.c. of permanganate must then be deducted from those used in the previous experiment. The test analyses are satisfactory.

L. DE K.

Method for the Differentiation of Organic Matter in Water. By A. G. WOODMAN (*J. Amer. Chem. Soc.*, 1898, 20, 497—501).—The process is based on the fact, already noticed by Barnes, that some organic matters are more readily oxidised by chromic acid than by permanganic acid.

In order to differentiate between the organic impurities of water, the author first uses Kubel's hot acid method, as follows. One hundred c.c. of the sample is mixed with 8 c.c. of dilute sulphuric acid (1:3), 10 c.c. of N/100 potassium permanganate is added, and the whole boiled for exactly 5 minutes; 10 c.c. of N/100 oxalic acid is added, and then titrated back with N/100 permanganate until the faint pink colour becomes permanent. To another portion of the sample, the chromic acid method is then applied. 6.2 grams of potassium dichromate is dissolved in distilled water, 50 c.c. of sulphuric acid added, and the solution diluted to 1 litre; 18 grams of ferrous sulphate is dissolved in 100 c.c. of sulphuric acid and 200 c.c. of water, and diluted to 500 c.c. Fifty c.c. of the sample is mixed with 20 c.c. of sulphuric acid, then with 10 c.c. of the chromic acid solution, and heated on the boiling water bath for 1 hour, the flask being covered with a watch-glass. Ten c.c. of the iron solution is added, the liquid is poured into 500 c.c. of cold water, and titrated with the permanganate solution. A blank experiment is, of course, made. The oxygen ratio is found by dividing the number of c.c. of permanganate used in the Kubel process by those used for the same amount of water in the chromic acid method.

The ratio for vegetable organic matters is over 0.6, whilst that of sewage matter falls considerably below that figure. L. DE K.

Estimation of Nitrites in Waters. By LUCIEN ROBIN (*J. Pharm.*, 1898, [vi], 7, 575—577).—The water should be clear, colourless, and free from hydrogen sulphide; 50 c.c. of the water is mixed with 2 c.c. of a 20 per cent. solution of pure potassium iodide, and after well shaking 2 c.c. of glacial acetic acid is added, the free iodine is then estimated by the aid of thiosulphate. The method is applicable to waters containing 0.1 mg. of nitrous acid per litre. J. J. S.

Estimation of Methane, Carbon Monoxide, and Hydrogen by Explosion, in Technical Gas Analysis. By WILLIAM A. NOYES and J. W. SHEPHERD (*J. Amer. Chem. Soc.*, 1898, 20, 343—345).—The authors point out the difficulty experienced in the direct estimation of carbon monoxide by means of cuprous chloride, and prefer to analyse the mixture by explosion. This may be done by exploding the unconsumed part of the added oxygen by means of added hydrogen.

A new form of pipette has been introduced which allows of the explosion taking place in a perfectly closed space. The water in the pipette is mixed with a little sulphuric acid, which greatly diminishes the solubility of carbonic anhydride. The outer end of the capillary tube of the Orsat apparatus has been fitted with a specially constructed small hydrogen generator in which the gas is generated from aluminium and aqueous potash.

If ordinary gas has to be tested, its carbonic anhydride is absorbed by

potash, its heavy hydrocarbons by fuming sulphuric acid, and its oxygen in an alkaline solution of pyrogallol. Atmospheric air is then introduced, the mixture exploded, and after ascertaining the amount of carbonic anhydride formed, hydrogen is admitted and the excess of oxygen estimated. Allowance must be made for the nitrogen contained in the air, which is assumed to contain 20.9 per cent. of oxygen. The method of calculation will be easily understood by analysts accustomed to this kind of work. L. DE K.

Examination of Eucalyptus Oil. By HELBING and PASSMORE (*Zeit. anal. Chem.*, 1898, 37, 404—405; from Helbing's *Pharmacolog. Record*, VIII.)—A eucalyptus oil for therapeutic purposes should be characterised by a high percentage of eucalyptol and the absence of volatile aldehydes, which would irritate the mucous membrane. The sp. gr. should be between 0.910 and 0.930 at 15°. Eighty per cent. of the oil should distil between 170° and 190°, and on cooling to 16°, 40—50 per cent. of eucalyptol should crystallise out. This, after washing with a little light petroleum and drying, should melt at 5° and boil at about 176°; its sp. gr. is between 0.922 and 0.924 at 15°, and in a 100 mm. tube it should not rotate the plane of polarised light more than half a degree in either direction. The first fractions of the distillate should be tested with sodium hydrogen sulphite for aldehydes and ketones. Of seven samples examined, one (French) contained no eucalyptol, and one (Californian) only 1.8 per cent. Another specimen (Spanish) contained much aldehyde. M. J. S.

Distillation of Dilute Aqueous Solutions of Ethylic Alcohol. Estimation of Alcohol therein. By MAURICE NICLOUX and L. BAUDUER (*Bull. Soc. Chim.*, 1897, [iii], 17, 424—427).—Three dilute solutions of alcohol (1:500, 1:1000, and 1:3000) were distilled, and the alcohol contained in the different fractions of the distillate was estimated. The results obtained are given in tabular form, and are also represented by curves. It appears that the rapidity with which the alcohol distils over increases with the dilution, the first fourth of the distillate from the most dilute solution (1:3000) containing practically the whole of the alcohol present, whereas, in the case of the 1:500 solution, about 7 per cent. of the alcohol remained in the retort after a third of the liquid had passed over. The first twentieth contained, in each case, about half the total alcohol present. The alcohol in still more dilute solutions (up to 1:10,000) may be estimated by distilling over a fourth part and then applying the volumetric process, based on the oxidation of the alcohol by potassium dichromate, which has been previously described by one of the authors (*Compt. rend. Soc. biol.*, [x], 3, 841). N. L.

Estimation of Small Quantities of Glycerol. By MAURICE NICLOUX (*Bull. Soc. Chim.*, 1897, [iii], 17, 455—458).—The author points out some errors which Bordas and de Raczkowski have made in the application of his process for the estimation of alcohol to the estimation of glycerol (*Abstr.*, 1897, ii, 193). When oxidised by excess of potassium dichromate and sulphuric acid, glycerol yields only carbonic anhydride and water, and not formic acid; the latter is im-

mediately oxidised by the chromic acid, even in very dilute solution. The standard chromate solution should theoretically contain 37.28 grams of potassium dichromate per litre, and not 48 grams as stated by Bordas and Raczkowski. This has been confirmed practically by experiments with pure glycerol; 1 c.c. of the solution is equivalent to 5 c.c. of a 0.1 per cent. solution of glycerol. N. L.

Quantitative Separation of Hemicellulose, Cellulose, and Lignin. Presence of Pentosans in these Substances. By WILHELM HOFFMEISTER (*Landw. Versuchs-Stat.*, 1898, 50, 347—362. Compare this vol., ii, 148).—The separation of the cellulose-like carbohydrates of sunflower husks, is described.

In order to ascertain the effect of dilute ammonia on the cellulose substances of lignin, a dried 5 per cent. caustic soda extract was extracted successively with 1, 2, 3, and 4 per cent. sodium hydroxide solution. Five grams of the 2 per cent. extract was then subjected to the action of ammonia vapour; the cellulose did not completely dissolve in 6 weeks. Cellulose insoluble in caustic soda (32 grams) was next extracted with ammonia, in a similar manner, for 10 days, dried, and weighed. 30.46 grams remained, which, when treated with 5 per cent. aqueous caustic soda, yielded 0.96 gram (= 3 per cent.) of hemicellulose.

When cellulose is dissolved in Schweizer's solution, the residue is, by repeated extraction with aqueous sodium hydroxide, completely converted into the soluble form. On evaporating the ammonia from the Schweizer's extract, at the ordinary temperature, and on a water bath respectively, different amounts of cellulose are obtained; more hemicellulose is obtained, by caustic soda, from the heated solution than from that which was not heated. In this operation, the pentosans are more influenced than the hexosans; pentosans are not always readily dissolved by caustic soda, and hexosans are frequently more or less readily dissolved. Both occur in lignin and are then undoubtedly indigestible. These points have to be considered in judging the digestibility of these carbohydrates.

A comparison of analyses of clover, at different periods, in the first and second years of growth, shows that both cellulose (Schweizer's extract) and lignin increase during the vegetative period. In the first year, there was an increase in both constituents. In the second year, the lignin alone increased to the end; the cellulose decreased at the end of June. In the first year, it seemed an absolutely as well as relatively greater amount of cellulose and lignin was produced than in the second year; this, however, requires confirmation. The amount of pentosans in the Schweizer extract was relatively greater in the second than in the first year, but decreased in the lignin more in the second year than in the first; this result is also given with reserve.

N. H. J. M.

Volumetric Estimation of Nitrated Derivatives of Phenols. By LEO SCHWARZ (*Monatsh.*, 1898, 14, 139—153).—The method originally suggested by Mohr for the estimation of acids by titrating the amount of iodine liberated by them from a mixture of an iodate and an iodide, is applicable to the estimation of the nitrated phenols

and some of their derivatives. In order to obtain an accurate result, the phenol must be heated with the mixture of iodate and iodide at 100°, in a closed vessel, for some time. Under these circumstances, it is found that tri- and tetra-nitro-derivatives yield satisfactory results independent of the duration of heating, experiments having been made with picric acid, trinitroresorcinol, trinitro- α -naphthol, 2:5:6-trinitrothymol, and tetranitrofluorescein. Dinitro-compounds, on the other hand, yield iodine substitution products when the heating is prolonged, and a low result is then obtained (2:4-dinitrophenol, 2:4-dinitro- α -naphthol, 3:5-dinitrocresol, 2:6-dinitrothymol, dinitrofluorescein, and 3:5-dinitrosalicylic acid). Finally, mononitrophenols so readily yield substitution products that they cannot be estimated in this way; paranitrophenoxyacetic acid, however, gives good results.

A. H.

Application of Alkaline Formalin in Quantitative Analysis. By LUDWIG VANINO (*Ber.*, 1898, 31, 1763—1765. Compare this vol., ii, 461).—Gold and silver may be conveniently estimated by precipitating the metals with an alkaline solution of formaldehyde.

Silver chloride is converted quantitatively into metallic silver by the agency of formaldehyde and caustic soda. In the case of silver bromide and iodide, the decomposition proceeds with greater difficulty, and is not complete.

M. O. F.

Generalisation of Legal's Reaction. By G. DENIGÈS (*Bull. Soc. Chim.*, 1897, [iii], 17, 381—382. Compare *Abstr.*, 1897, ii, 467).—The author acknowledges the claim of Béla von Bittó (*Abstr.*, 1892, 924) to priority in the study of the nitroprusside reaction for aldehydes, &c., and draws attention to certain points of difference between his own work and that of von Bittó, with whose conclusions he is in general agreement.

N. L.

Analysis of Crude Tartars, &c. (*Zeit. anal. Chem.*, 1898, 37, 382—384. See this vol., ii, 465).—The chemists at the factory "late Goldenberg, Geromont and Co." have introduced the following modifications into their process. The mixture of lees with hydrochloric acid is diluted with an equal volume of water after the first hour's digestion, and then allowed to remain for a second hour before making up; the evaporated filtrate is treated with acetic acid while hot instead of first cooling: after stirring for 5 minutes, the alcohol is added immediately, thus avoiding the precipitation of slimy substances which would obstinately retain acetic acid. The washing is prolonged until 30 c.c. of the filtrate requires only 2—3 drops of N/5 alkali to render it alkaline, the indicator used in the titration being a sensitive litmus paper of reddish-violet colour. In all other respects, the details of the former method are retained.

M. J. S.

Detection and Separation of Admixed Tartaric, Racemic, and Mesotartaric Acids. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, 17, 69—75). See this vol., i, 515.

Estimation of Succinic Acid in the Presence of Tartaric and Lactic Acids. By FRED. BORDAS, JOULIN and SIG. DE RACZKOWSKI (*J. Pharm.*, 1898, [vi], 7, 417—418).—The solution containing the three

acids is exactly neutralised with N/10 potassium hydroxide, an excess of a concentrated solution of silver nitrate added, and the precipitate removed and washed until the filtrate no longer gives a precipitate with potassium chromate. The precipitate consists of silver succinate, all the silver tartrate having been dissolved by the water. The precipitate is washed into a flask with water, one or two drops of potassium chromate solution added, and N/10 sodium chloride run in until the red colour of the precipitate disappears and the liquid becomes slightly yellow; the solution is finally titrated back with N/10 silver nitrate.

J. J. S.

Volumetric Estimation of Glycerophosphates. By H. IMBERT and J. PAGÈS (*J. Pharm.*, 1898, [vi], 7, 378—384).—It is stated that the method adopted by Imbert and Astruc is general and sufficiently accurate. By the use of calcium chloride, phosphates may also be estimated in the presence of glycerophosphates, especially if the amount of phosphate present is more than 5 per cent. of the mixture. Below this limit, the method is not so trustworthy. Borates and silicates must be detected by a special analysis.

J. J. S.

Estimation of Rosin and Rosin Oil in Linseed Oil. By LEONARD DE KONINGH (*Chem. News*, 1898, 77, 287).—McIlhiney (*Abstr.*, 1894, ii, 370) has shown that boiled linseed oil, when treated with bromine, yields no hydrogen bromide, but that a large quantity of this acid is formed when the oil contains rosin or rosin oil. In order to make this a practical process for the assay of linseed oil, the author first takes the bromine-acidity figure of the sample, and if it is fairly high, there is no doubt that rosin, rosin oil, or both are present. Another portion of the sample is now saponified with alcoholic potash and any unsaponifiable matter is extracted by means of light petroleum; if any appreciable quantity is obtained, the bromine-acidity figure is taken, which then will simply represent rosin oil. Rosin oil, as it occurs in England, contains but very little saponifiable matter, but samples from German origin contain much more of the rosin acids, and will, therefore, be only partially recovered by the alkali-petroleum treatment.

Rosin cannot be estimated by isolating the fatty acids from the extracted soap-ley, and subjecting them to the bromine treatment, as, even when free from rosin, they yield an appreciable quantity of hydrogen bromide. If the sample of linseed oil should contain free fatty acids, it will, of course, yield a trace of hydrogen bromide.

If rosin should be found, it may to some extent be derived from the use of inferior rosin oil. If the oil contains no mineral matter, the presence of added rosin becomes very doubtful.

L. DE K.

Analysis of Theobromine. By MAURICE FRANÇOIS (*J. Pharm.*, 1898, [vi], 7, 521—523).—The following tests are recommended. A solution of theobromine in nitric acid and water yields a precipitate with a 10 per cent. solution of silver nitrate; on warming and then allowing to cool, colourless needles are deposited.

The formation of theobromine tetriodide is another good test. Also treatment with bromine water and subsequent addition of ferrous

sulphate and ammonia, when an indigo blue colour is developed ; this last reaction is also given by caffeine.

For analysis, the best methods are. 1. Heating in a platinum vessel ; no residue should be left. 2. Melting point determination (338—340°). 3. Determination of solubility in alcohol of 95°. The solubility of theobromine at 21° is 0.045 gram in 100 c.c. of alcohol, whereas for caffeine the amount is 0.93 gram in 100 c.c. If theobromine contains 5 per cent. of caffeine, 100 c.c. of alcohol dissolves 0.29 gram of the mixture. J. J. S.

Chemico-legal Detection of Vegetable Poisons. By MICHAEL VON SÉNKOWSKI (*Zeit. anal. Chem.*, 1898, 37, 359—365).—The author is unable to confirm unconditionally the statement of Kippenberger (Abstr., 1895, ii, 465) that glycerotannic acid effects an universal separation of the vegetable alkaloids from the products of decomposition of animal matter. Solutions of peptone (Witte's) and of coelichicine and helleborein behave almost identically with that reagent, giving no precipitate until water is added. Concentrated glycerotannic acid dissolves even albumin. The alkaloid tannates are, however, not completely insoluble in water, and when brought in contact with hide powder the tannic acid is completely removed from them, leaving the alkaloid in solution. With proteids, this is not the case ; they remain entirely in the precipitate. An aqueous extract of cadaveric matter, acidified with tartaric acid, is therefore precipitated by a 10 per cent. solution of tannic acid (which must be as free as possible from gallic acid) using as small an excess as possible ; about 10—15 c.c. to 100 grams of a substance is generally sufficient. Hide powder is then immediately added in quantity sufficient to render all the tannic acid insoluble, and after a few hours the whole is thrown on a filter. A clear and almost colourless filtrate is obtained, which is ready for extraction with ether or chloroform. Care must be taken to keep the mixture acid during the whole operation, otherwise part of the alkaloid may remain in the precipitate. It is also advisable to shake the filtrate with light petroleum before using the alkaloid solvent, otherwise the alkaloid may be contaminated with traces of fat.

M. J. S.

Estimation of Alkaloids in Tinctures. By JULIUS KATZ (*Arch. Pharm.*, 1898, 236, 81—100).—By the following methods of estimating the amount of alkaloids in tinctures, &c., the author avoids the application of heat which causes the decomposition of many alkaloids. To 25 c.c. of the tincture containing about 45 per cent. of alcohol, 1 c.c. of a 33 per cent. solution of sodium carbonate is added, and the alkaline solution shaken with 50 c.c. of ether. The ethereal extract is washed with 3 c.c. of water, the alkaline solution extracted twice with successive quantities of 25 c.c. of ether containing 10 per cent. of alcohol, and the extracts washed separately with 1.5 c.c. of water. The mixed ethereal solutions are shaken with 2—3 grams of ignited calcium sulphate, filtered into a flask containing 50 c.c. of water, and then titrated by Partheil's method with centinormal acid, using 3 drops of an alcoholic solution of iodeosin (1:250) as indicator. In the case of tinctures containing alkaloids which are not easily soluble

in ether, 25 c.c. is extracted with 30 c.c. of a mixture of 3 parts of chloroform with 1 of ether, the extract washed with 3 c.c. of a 30 per cent. solution of sodium chloride, and the process repeated twice, using 15 c.c. of the solvent and 1.5 c.c. of salt solution each time. If necessary, the separation of the chloroform-ether from the aqueous solution may be accelerated by adding 2—3 grams of sodium chloride. The mixed extracts are run into 10—15 c.c. of a 10 per cent. solution of sodium chloride and titrated as before.

Tinctures which contain more than 45 per cent. of alcohol are diluted with water, or when chloroform and ether are to be used, with a 15 per cent. solution of sodium chloride. Preparations containing chlorophyll or fat are shaken with an equal weight of water acidified with a few drops of sulphuric acid and then filtered; the last traces of fat are removed by shaking with light petroleum. The author finds that the alkaloid cannot be completely removed by the above methods from aqueous extracts which contain more than 3 per cent. of the alkaloid, possibly on account of their high content of pectin. 1—1.5 grams of extract is dissolved in 40—50 c.c. of 45 per cent. alcohol, and the alkaloid then estimated as in the case of a tincture. Estimations of aconitine, atropine, hyoscyamine, coniine, emetine, and of the alkaloids in a number of homœopathic essences and extracts are quoted.

E. W. W.

Estimation of Plant-food in Soils. By WALTER MAXWELL (*J. Amer. Chem. Soc.*, 1898, 20, 107—109).—This is a preliminary note on the best solvents for using in the testing of soils for agricultural purposes. Carbon acids and amido-acids only should be used; mineral acids should be excluded.

L. DE K.

Method of Drying Fæces. By HEINRICH PODA (*Zeit. physiol. Chem.*, 1898, 25, 355—359).—The chief point in this method, which is described as easy and rapid, consists in performing the desiccating process after the mass has been treated with absolute alcohol.

W. D. H.

The Estimation of Hæmoglobin in Cat's Blood. By FRIEDRICH KRÜGER (*Zeit. physiol. Chem.*, 1898, 25, 256—257).—The statement made by Abderhalden (this vol., ii, 415) that cat's hæmoglobin is difficult to crystallise is disputed. His quantitative results also are criticised, as no spectrophotometric observations were made.

W. D. H.

General and Physical Chemistry.

Spectra of some of the Elements with a Constant Luminous Discharge in Geissler Tubes. By ALFRED KALÄHNE (*Ann. Phys., Chem.*, 1898, [ii], 65, 815—848).—The spectra of iodine, bromine, mercury, cadmium, sodium, tin, and lead were examined under a constant discharge from 600 accumulator cells, giving an E. M. F. of 1200 volts. The appearances obtained were qualitatively similar to those which are given by weak, intermittent discharges. The proportionality between light intensity and current strength which Ångström noticed with nitrogen and hydrogen, was not observed with mercury or cadmium vapour. In the case of cadmium, the intensity of the lines increases more rapidly, with mercury less rapidly, than the current strength. With a constant current, the lines in the mercury and cadmium spectra decrease in intensity with increasing pressure. H. C.

Racemic Substances. By FRIEDRICH W. KÜSTER (*Ber.*, 1898, 31, 1847—1853).—Landolt (*Optische Drehungsvermögen*, 2nd ed.) concludes that racemic (*r*) compounds only exist in the crystalline state; in the liquid state and in solution, they are entirely dissociated into their dextrorotatory (*d*) and lævorotatory (*l*) components. This, however, is not universally true; for instance, 100 parts of water dissolve only 0.684 parts of silver *l*-valerate, but 1.182 of the *r*-salt. Taking the electrolytic dissociation into account, it can be shown that the solution of the *r*-valerate would be supersaturated as regards the *l*-salt, supposing it to be dissociated entirely into its components. The discrepancy can only be explained by supposing that part of the *r*-salt remains in the racemic condition, even after it has gone into solution; this part can be calculated to be at least 20 per cent. of the whole. A similar supposition must be made with regard to barium camphoronate, of which the *d* and *l* varieties are very sparingly soluble, whilst the *r* variety dissolves very readily. To take the case of a liquid, it is possible to calculate, from the known solubility of *d*-coniine (1.80 parts in 100 of water at 19.5°) what would be the solubility of *r*-coniine, assuming the latter liquid to be simply a (*dl*) mixture of *d* and *l* components. The solubility thus calculated is considerably greater than that actually observed (1.93 parts); this could be accounted for by supposing not less than 30 per cent. of the liquid *r*-coniine to exist still in the racemic condition, or about 15 per cent., if it be assumed that the active coniines are also associated each into double molecules. C. F. B.

Action of Ammonium Persulphate on the Silver of Photographic Plates. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE and ALPHONSE SEYEWETZ (*Compt. rend.*, 1898, 126, 1639—1642).—The use of a 5 per cent. aqueous solution of ammonium persulphate is recommended for

the correction of over-exposed and over-developed photographic plates, this reagent having the advantage over other reducers of preserving the half-tones. It appears that the ammonium persulphate penetrates the gelatin film and dissolves the silver deposited in its lower layers, a soluble double sulphate of silver and ammonium being formed. The latter diffuses through the film and, on reaching the surface, is reduced by the excess of ammonium persulphate with which it there comes in contact, with evolution of oxygen and deposition of metallic silver. This deposition compensates to some extent for the solution of silver taking place in the interior of the film, but since the former process occurs only at the surface, whilst the latter is confined to the deeper parts of the film, it follows that the superficial half-tones are but little affected whereas the deeper and denser deposits are considerably reduced.

N. L.

Radiations from Thorium and its Compounds. By GERHARD CARL SCHMIDT (*Compt. rend.*, 1898, 126, 1264).—Thorium and its compounds emit radiations analogous to those emitted by uranium and its compounds; they discharge an electrified body whatever the sign of the charge, and the effect is exerted through a thin sheet of aluminium. The nitrate and sulphate are more active than the oxide.

C. H. B.

Electrical Oscillations. By HUGO KAUFFMAN (*Zeit. physikal. Chem.*, 1898, 26, 719—727).—When the vapours of various chemical compounds are exposed to the influence of electrical oscillations, various results may occur: (1) the vapour may become luminous; (2) it may be crossed by spark discharges, usually of a green colour; (3) it may remain dark, at least until a very high tension is reached. The behaviour in this respect of over 50 compounds was investigated, and, although general deductions cannot be drawn from so few observations, yet some constitutive influences are indicated. Thus, almost all the aromatic amines become luminous, and present more or less similar appearances, whilst the ease with which luminosity occurs appears to be in part dependent on the basic character of the amine, as compounds which, by substitution, have lost their basic nature (for example, nitraniline or tribromaniline) are no longer rendered luminous. This rule, however, cannot be extended to cyclic compounds containing nitrogen. Amongst hydrocarbons, the aliphatic compounds and the simple benzene compounds remain dark until a very high tension is reached; but most of the hydrocarbons containing two or more benzene rings readily become luminous. In all cases, it was observed that, during luminosity, the vapour acted as a conductor.

L. M. J.

Mercury-zinc and Mercury-cadmium Cells as Standards. By WILHELM JAEGER and K. KAHLE (*Ann. phys. Chem.*, 1898, [ii], 65, 926—942).—A comparison of a series of Clark standard cells with cells of the Weston type has been made during a period of over twelve months, in order to test the constancy of these cells. The mean of the results obtained is given below.

Date	Clark 0°. Cadm. 20°.	Clark 15°. Cadm. 20°.	Clark 0°. - Clark 15°.
March, 1896	1.4227	1.4066	0.0164 int. volt.
Jan., 1897	1.42277	1.40676	0.01631 „
Nov., 1897	1.4228	1.40660	0.01650 „
Mean	1.42277	1.40663	0.01642.

H. C.

Efficiency of an Electrolytic Cell. By FERDINAND HURTER and B. ZAHORSKI (*J. Soc. Chem. Ind.*, 1897, 16, 97—107).—A formula which expresses the efficiency of an electrolytic cell, or that fraction of the energy consumed by the cell which is converted into the desired potential chemical energy, is ae/V . Here e is the so-called back E. M. F. corresponding to the products which are desired, and V the actual E. M. F. measured at the terminals of the cell. The factor a is the fraction of the electrochemical equivalent of the desired substance actually obtained per ampère. Theoretically, for every ampère of current, one electrochemical equivalent should be obtained, and this theoretical yield is easily approached in all cases where the separated ions are deposited as solids or removed as gases. But where the products of electrolysis remain in solution, the newly-formed products take part in the conduction of the current, some of which therefore is wasted. To make a satisfactory calculation of the exact value of the current efficiency, it is therefore necessary to know how the current divides between several electrolytes. This, as Hittorf has pointed out, can be found by migration experiments, and current efficiency depends chiefly on the phenomena of migration, or, what is practically the same thing, the conductivity of the solutions. As the authors show, a limiting value of the current efficiency can, therefore, be calculated, but in most cases this is all, as in complicated processes we know but little of the real values of the E. M. F. of polarisation. H. C.

Chemical Theory of the Lead Accumulator. By F. DOLEZALEK (*Ann. phys. Chem.*, 1898, [ii], 65, 894—920).—The simplest theory of the changes occurring in the lead accumulator is expressed by the equation $\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{PbSO}_4 + 2\text{H}_2\text{O}$. On charging, the reaction occurs from left to right, on discharging, from right to left. This process would be a fully reversible one, but many of the changes which occur in the accumulator when at work are not apparently in keeping with this simple view of its action; this is more especially the case with the behaviour on charging and discharging, as the E. M. F. is found to be slightly higher during the first than during the second operation, thus causing a considerable loss of energy. The author traces this loss to the changes which take place in the concentration of the acid, and consequent diffusion and convection, and also production of concentration currents in the cell. Taking these changes into account, the above theory of a fully reversible reaction in the sense given is fully satisfactory. H. C.

New Electrolytic Diaphragm. By HEINRICH PAULI and LUDWIG PINCUSOHN (*Chem. Zeit.*, 1897, 21, 1048—1049).—The improved cell recommended by the authors is made much shorter and wider than the

ordinary commercial porous pot. At its upper end, it is strengthened by a flange containing four holes, through which two wires are passed, and in this manner the cell is suspended within the outer vessel, such as a flat crystallising pan. As the electrodes are not curved, but straight and parallel, it is easier to keep up a uniform current density.

L. DE K.

Accuracy of the Values of Dissociation Determined by the Electrical Conductivity Method. By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1898, 26, 699—710, and *J. Amer. Chem. Soc.*, 1898, 20, 517—528).—Van Laar considers that the conductivity method does not give accurate values for the dissociation (this vol., ii., 158); the author is of a contrary opinion, and shows that, in some particulars, the expressions deduced by van Laar for the heat of dissolution are inaccurate, and deduces formulæ based upon both Ostwald's and van't Hoff's dilution laws. The values, as calculated by these expressions, especially in the case of the second, agree well with the experimentally found values in the cases of those compounds where van Laar had found that discrepancies occur between the determinations and the values deduced by his formula. The fact that the inversion velocities of sugar by hydrogen chloride differ in water and in aqueous alcohol (Cohen, this vol., ii, 154), although the dissociation as determined by the conductivity is equal in the two solvents, does not disprove the availability of the conductivity method, as the alcohol may have a catalytic retarding influence on the reaction itself, whilst, further, the experiments of Lowenherz actually indicate a lowering of the dissociation in aqueous solutions on the addition of alcohol (Abstr., 1896, ii, 587). The conductivity dissociation values for potassium chloride in from N/100 to N/10 aqueous solutions are in very close accord with those determined cryoscopically by Jones, Loomis, Abegg, and Raoult, whilst for sodium chlorides the values do not differ more from the mean of the cryoscopic results than do the latter among themselves. The author, therefore, considers that the conductivity method does actually yield the true dissociation, and further points out that, even if van Laar's contention were supported, his explanation fails, inasmuch as it necessitates that the dissociation values should alter with the current strength, which is not the case.

L. M. J.

Electrical Conductivity of Potassium Permanganate Solutions. By GEORG BREDIG (*Compt. rend.*, 1898, 126, 1269).—Measures of the electrical conductivity of dilute solutions of potassium permanganate have been made by the author (*Zeit. physikal. Chem.*, 1893, 12, 233, and 1894, 13, 217, and by Franke and Loven, *ibid.*, 1895, 16, 475, and 1896, 7, 376. Compare Legrand, this vol., ii, 496).

C. H. B.

Conductivity of Aqueous Solutions of Praseodymium and Neodymium Sulphates. By HARRY C. JONES and H. M. REESE (*Amer. Chem. J.*, 1898, 20, 606—607).—The following table gives the conductivity of aqueous solutions of the salts for various concentrations; v denotes the number of litres of solution which contain a gram molecule of the salt, and μ_v the corresponding molecular conductivity.

Praseodymium sulphate.		Neodymium sulphate.	
v .	μ_v	v .	μ_v
14.71	98.33	25.33	115.03
29.42	117.43	50.65	137.65
58.84	141.42	101.31	166.35
117.68	169.47	202.62	197.91
294.2	217.83	506.5	255.43
588.4	262.65	1013.0	303.45
1176.8	317.10	2026.0	366.0
1471.0	331.43	2532.6	382.9
2942.0	403.37	5065.2	462.5
5884.0	482.61		

W. A. D.

Determination of Transference Ratios by Electrolysis of Dilute Salt Solutions. By WILLI BEIN (*Zeit. physikal. Chem.*, 1898, 27, 1—54).—The work of previous observers is discussed at considerable length with especial reference to the influence of diffusion on the values obtained. The method used by the author is the general one of the analysis of the anodic, mean, and cathodic liquids, but various forms of apparatus were employed according to the dilution of the electrolyte and the temperature required; all these are described, and numerous figures are given. For sodium and hydrogen chlorides, the values were found to be almost independent of the concentration, but to vary with the temperature, the transference numbers for the anions being given by the expressions: HCl , $n_t = 0.157 + 0.0009t$; NaCl , $n_t = 0.622 - 0.00074t$. For potassium chloride, the values $n_{11} = 0.503$ and $n_{76} = 0.513$ were obtained, and appeared to be independent of concentration, at least between the limits of $\text{N}/5$ and $\text{N}/100$. For lithium chloride, the values $n_{20} = 0.624$ and $n_{97} = 0.621$ were obtained in $\text{N}/100$ solutions, and $n_{25} = 0.672$; $n_{96} = 0.610$ for $\text{N}/5$ to $\text{N}/20$ solutions. For ammonium chloride, rubidium chloride, caesium chloride, and thallium chloride, the values 0.507, 0.515, 0.508, 0.516 were respectively obtained at about 20° . Calcium chloride gave results similar to those obtained for lithium chloride, the transference ratios changing but slightly with dilution at high temperatures: thus $n_{22} = 0.553$, $n_{96} = 0.530$ for $\text{N}/100$ solution, and $n_{22} = 0.608$ for n_4 solution. For barium chloride, $n_{10} = 0.559$ and $n_{97} = 0.515$ in solutions containing 0.04 per cent. chlorine, and $n_{12} = 0.583$, $n_{97} = 0.554$ in solutions containing 0.78 per cent. chlorine. For cadmium chloride, $n_{22} = 0.568$ and $n_{96} = 0.473$ in solutions with 0.2 per cent. chlorine, but at higher concentrations the temperature change was much less. Silver acetate gave the values $n_{24} = 0.413$ and $n_{96} = 0.439$, which, however, do not agree with the results of Nernst and Hittorf. Sulphuric acid gave numbers in accord with the expression $n_t = 0.160 + 0.0015t$, and these also differ from Hittorf's values. For copper sulphate, the values vary slightly with concentration and temperature, and apparently give a maximum of 0.632 at 15° , for silver nitrate, $n_{76} = 0.517$ changing but slightly with temperature. The remaining determinations were all made at temperatures of about 20 — 25° with the following results.

Salt.	<i>n</i> .	Salt.	<i>n</i> .
Strontium chloride	0·560	Thallium sulphate	0·528
Magnesium chloride	0·615	Magnesium sulphate	0·541
Manganese chloride	0·613	Sodium carbonate	0·600
Cupric chloride	0·595	Potassium carbonate	0·435
Cobalt chloride	0·585	Sodium hydroxide	0·799
Sodium bromide	0·625	Ammonium hydroxide	0·562
Potassium iodide	0·505	Calcium hydroxide	0·786
Hydrogen nitrate	0·172	Potassium permanganate	0·559
Sodium nitrate	0·629	Hydrogen succinate	0·239
Hydrogen oxalate	0·214		

Some determinations were also made in the case of solutions of concentration from 3N to 4N. The values obtained differ very considerably, however, from those at low concentrations, and exhibit a much more marked temperature change; for example, HCl (13·94 per cent. Cl), $n_{97} = 0·393$; NaCl (12 per cent. Cl), $n_{20} = 0·677$; CdCl₂ (13·8 to 13·6 per cent. Cl), $n_{24} = 0·657$, $n_{97} = 0·960$; CaCl₂ (14 per cent. Cl), $n_{25} = 0·718$; CoCl₂ (9·7 per cent. Cl), $n_{25} = 0·737$, $n_{97} = 0·79$. L. M. J.

Dissociation of Water. By R. A. LEHFELDT (*Zeit. physikal. Chem.*, 1898, 27, 94).—Luther has calculated recently (this vol., ii, 422) that, at 20°, the concentration of free hydrogen in water vapour is $10·10^{-27}$ gram-molecules per litre. The author considers such determinations to be of no value whatever, and points out that, assuming the mass of the molecule of hydrogen to be $1·6 \times 10^{-24}$ (Nernst), Luther finds that 1 molecule of hydrogen is present in 80 litres. L. M. J.

Relation between Solubility and the Heat of Formation of Electrolytes. By GUIDO BODLÄNDER. (*Zeit. physikal. Chem.*, 1898, 27, 55—74).—The electromotive force required to separate the ions of a salt in a saturated solution is given by the equation $E_s = E_a + E_k - 0·058 \log p^{\frac{1}{n_a} + \frac{1}{n_k}}$ where n_a and n_k are the valencies of the ions, E_a , E_k are the E.M.F. necessary to separate the anion and cation respectively in normal solutions, and p is the solubility in equivalents. The values for E_a and E_k have been given by Nernst and Neumann (*Abstr.*, 1894, ii, 373; 1897, ii, 394), so that from E_s the value of p can be derived, and *vice versa*. Since the heat of formation of the compound is approximately proportional to E_s and is given by the equation $Q = 230E_s$, the relation between p and Q is obtained. The first set of compounds investigated were the iodides, and the calculated values for the solubility are compared with the experimental numbers. In this set, the agreement, although far from exact, was fairly satisfactory, but for the bromides and chlorides the calculated numbers can only be said to be of the same order of magnitude as the actual values. For the fluorides, the value of E_a is not known, but is calculated from the solubility of silver fluoride; from this, the solubilities of other fluorides are derived with fair agreement with experimental numbers. For the sulphides, the actual solubilities were not calculated, but the order must be that of

the differences $E_k - E_s$, and the order so obtained agrees, with few exceptions, with the known chemical properties of the sulphides. For the hydroxides, the value of E_a is obtained from the solubility of lead hydroxide, and from this, the values for the solubility of other hydroxides; here satisfactory results were obtained, but this was not the case with the sulphates. Assuming the formula to be accurate, the heat of formation is calculated from the solubility in the case of some iodides, and from the difference between the value thus obtained and the value found, the author deduces the temperature coefficient of the E.M.F., but it is doubtful whether any value really attaches to these numbers. It is seen from the expression given that the following law holds in the case of slightly soluble salts; for salts of different acids with the same metal, the solubility increases with the tendency of the acid radicle to pass from the electrically neutral to the ion state; a similar law holds for salts of different metals with the same acid, and examples are adduced. In the case of two salts with the same cation, the solubility of the first must be greater or less than that of the second according as $(E_a - E_a')$ is greater or less than $(E_s - E_s')$. In the case of bromides and chlorides, therefore, where $(E_s - E_s') > 85 \cdot 1/230 (= E_a - E_a')$ the bromide is the more soluble, and this is found to be in accord with the facts, a similar application to the salts of silver and sodium also giving valid results. L. M. J.

Law of Thermal Constant. By DONATO TOMMASI (*Bull. Soc. Chim.*, 1897, [ii], 17, 438—440).—In his work on the thermochemistry of mercury salts (Abstr., 1896, ii, 648), Varet finds that these salts conform to the law that the replacement of one metal by another in solutions of their salts always gives rise, in the case of any two metals, to the same heat change, no matter what acid radicle is present. This law Varet attributes to Andrews, and Favre and Silbermann, but the author claims to have been the first to enunciate it in 1882. H. C.

Cryoscopic Measurements. By A. PONSOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 395—405).—Four series of cryoscopic determinations were made with dilute sugar solutions, every precaution being taken to eliminate error. The molecular reductions found were 19·01, 18·50, 18·725, and 18·97. The value, calculated by the van't Hoff formula is 18·77. H. C.

Transition Temperature of Sodium Sulphate. A New Fixed Point in Thermometry. By THEODORE W. RICHARDS and JESSE BRIGGS CHURCHILL (*Zeit. physikal. Chem.*, 1898, 26, 690—698).—The transition temperature of the change $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ is considered to be a very suitable fixed temperature for thermometry, and the following are the advantages claimed by the authors. The salt can be readily obtained in a state of sufficient purity, as after two crystallisations further purification has practically no effect on the transition temperature, which is also unaffected by pressure, whilst, further, the temperature of an outer bath has very little influence if the temperature of the above direct action is taken, namely, that of the melting of the hydrate. Very careful determinations gave the temperature as $32 \cdot 484^\circ$, and it was found that no extraordinary

care is requisite in order to get values correct to 0.01° . This temperature is 32.379° on the hydrogen scale, and is near the point of maximum difference between the two scales. The authors also consider it probable that other transition points will be found suitable for thermometric fixed temperatures.

L. M. J.

Tables for the Reduction of Boiling Points to Normal Pressure. By PAUL FUCHS (*Zeit. angew. Chem.*, 1898, 869—871).—Useful tables are given of the boiling points of some liquids at pressures varying from 710—780 mm; the list includes acetone, alcohol, aniline, benzene, methylic alcohol, bromobenzene, chlorobenzene, and metaxylene.

L. DE K.

Vapour Pressure Measurements. II. By GEORG W. A. KAHLBAUM (*Zeit. physikal. Chem.*, 1898, 26, 577—658. See Abstr., 1894, ii, 131).—[With P. SCHROETER and C. G. VON WIRKNER].—The authors first show that when a liquid is boiled under reduced pressure, the actual pressure in the boiling flask is equal to that measured at the end of the condenser.

[With EMIL TOENNIES and C. G. VON WIRKNER].—The vapour tension determinations by the dynamical method were subjected to severe tests, measurements by different observers at different times being compared; separate curves were also constructed for the same set of determinations, in order to see whether errors arise from the method of plotting and interpolation. In all cases, the concordance is very complete, so that the dynamical determinations are trustworthy, a result also confirmed by the fact that the differences between the boiling points of benzene, toluene, and water at pressures varying from 35 mm. to 760 mm. exhibit no *irregular* variations, but change continuously.

[With C. G. VON WIRKNER].—The series of fatty acids were first investigated, and the boiling points compared at a large number of pressures varying from 10 mm. to 760 mm. The values were compared with those calculated from the boiling points of water and of propionic acid by Dühring's law. In all cases, the determinations differ from the calculated values, but the differences are less when the values are deduced from propionic acid than when they are obtained from water. Dühring's law, therefore, although of use in such cases, cannot be regarded as an absolute natural law. The differences between the boiling points of the whole series (C_1 to C_{10}) at the various pressures are compared; in the cases of formic and acetic acids, and of nonoic and decoic acids, the difference is independent of pressure, so that the boiling point curves are parallel; the curves of acetic acid and propionic acid, however, diverge with falling pressure, but in all the other cases the curves approach as the pressure falls. A number of benzene derivatives containing a phenyl group were next examined, and the determinations agree well with those of Ramsay and Young, and other observers, where comparable data are available. The boiling points at 760 mm. ascend in the following order. Benzene, bromobenzene, benzaldehyde, phenol, aniline, benzonitrile, benzylic alcohol, nitrobenzene, benzoic acid; but at 6 mm. the order becomes benzene, bromobenzene, benzaldehyde, benzonitrile, aniline, phenol, nitrobenzene, benzylic alcohol, benzoic acid; so that the boiling point

curves intersect in the cases of the following pairs, benzonitrile-aniline, benzonitrile-phenol, aniline-phenol, benzylic alcohol-nitrobenzene. The only previously known case of the intersection of vapour pressure curves was that of benzene-ethyl alcohol.

[With C. WICHROWSKI and THEODOR TESSE.]—The vapour pressure determinations of aniline, and its methyl, ethyl, dimethyl, and diethyl derivatives were made at pressures varying from 5 mm. to 760 mm. The boiling points of aniline and dimethylaniline approach with falling pressure, as do those of methylaniline and ethylaniline, whilst those of methylaniline and dimethylaniline diverge, so that the boiling point curves for aniline and methylaniline, and for dimethylaniline and ethylaniline are approximately parallel.

[With THEODOR TESSE.]—Schröder has formulated the rule that the substitution of the groups $-\text{CO}\cdot\text{CH}_3$, $-\text{COOCH}_3$, and $-\text{COCl}$ for hydrogen lead to equal changes of the boiling point. The boiling points were, therefore, determined between 1 mm. and 760 mm. in the cases of acetophenone, benzoic chloride, and methyl benzoate. Schröder's rule is not found to be valid, as, although the difference between the boiling points of the two latter compounds at 760 mm. is only 0.4° , yet at 10 mm. it is 3.5° , when the difference between those of the two first compounds is 5.2° .

[With EMIL TOENNIES.]—A number of position isomerides were next investigated, chiefly toluene derivatives, namely, ortho-, meta-, and para-cresol; ortho-, meta-, and para-toluidine; ortho- and para-dimethyltoluidine; ortho- and para-nitrotoluene. In the case of the cresols, the para-compound has throughout the whole range of pressure a boiling point about 0.5° higher than that of the meta-compound, and 11.2° higher than that of the ortho-compound. A similar constant difference in the boiling points occurs in the case of the toluidines, so that for each of these sets of compounds Dalton's law holds. This is not the case, however, in the dimethyltoluidines, nor in the nitrotoluenes, and for these compounds there is a much greater difference in the actual boiling points, so that the law probably only holds for a set of isomerides the boiling points of which are sufficiently near.

[With KURT ARNDT.]—Trimethylene bromide and propylene bromide exhibit a difference of boiling point which increases with pressure, and the same obtains for the ortho- and meta-chloranilines. The boiling point curves of chloro- and bromo-naphthalenes approximate closely at low pressures, so that, whereas the difference in the boiling points at 760 mm. is about 22° , at 1.5 mm. it is only 8° .

The author discusses the bearing of the determinations on the generally accepted relationships between constitution and boiling point, and points out that these can have no real significance, as different relations are found when the boiling points are taken at pressures other than 760 mm. Comparisons in the benzene series indicate that throughout all pressures, substitution produces a greater effect in a benzene group than in a toluene group, and that the boiling point pressure curves are flatter for simple compounds than for complex, although a few exceptions occur; this the author considers to be due to greater cohesion among the simpler molecules. A comparison of the curves for a large number of compounds shows that, in general,

those of the fatty compounds are flatter than those of aromatic compounds of approximately equal boiling points, and that, with a solitary exception, no curve of a fatty compound is parallel to that of any aromatic compound, although parallelism frequently occurs between two fatty compounds or two aromatic compounds. The presence of the hydroxyl group appears also to have an influence in causing flatness of a curve, but, on the whole, the author allows that little can be deduced, in the positive sense, from the great accumulation of data.

[With KURT ARNDT.]—Comparisons were made between the decrease of the boiling point between 760 mm. and 10 mm. on the one hand, and the molecular dispersion, as measured by Lorenz's formula, on the other. For this purpose, the latter constant had to be determined for some of the compounds, chiefly aniline derivatives. In a very large number of cases, it is evident that an increase in the one constant is accompanied by an increase in the other, the number in which this is the case being too great to be ascribed to mere coincidence, especially when the comparison is made between allied compounds with different dispersions, or between compounds of different boiling points but equal boiling point change, and also equal dispersion. Nevertheless, many exceptions occur, the most noteworthy being the series of fatty acids, where, although the boiling point decrease is practically constant, yet the molecular dispersion continuously increases. In this case, however, the actual dispersion is approximately constant, and although the author offers no explanation, he considers that a real connection between the two constants is indicated. L. M. J.

Thermochemical Data for Ethylmalonic Acid and its Isomeric, Glutaric and Methylsuccinic Acids. By GUSTAVE MASSOL (*Compt. rend.*, 1898, 126, 1354—1355).—Ethylmalonic acid melts at 111.5° and dissolves in water with absorption of heat (-2.96 Cal.). The heats of neutralisation for the first and second molecules of potash are $+14.08$ and $+13.80$ Cal. respectively, both acid and base being in solution. The normal potassium salt dissolves in water with development of 4.45 Cal., and its heat of formation from the solid acid and base is $+48.25$ Cal.; comparison of the latter figure with the corresponding numbers for methylsuccinic acid, $+45.18$ Cal., and glutaric acid, $+44.23$ Cal., shows that the heat of formation of the normal salts of the three isomeric acids decreases progressively with increase of the distance between the carboxyl groups. A similar relation is observed in the case of the three phthalic acids. N. L.

Heat of Neutralisation of Phenylphosphoric Acid. By G. BELUGOU (*Compt. rend.*, 1898, 126, 1575—1576).—Phenylphosphoric acid is prepared by the action of phosphoric anhydride on phenol, the diphenylphosphoric acid that is formed at the same time being removed by washing with ether, and the excess of phosphoric acid by fractionally precipitating the aqueous solution with lead acetate. The heat of neutralisation by sodium hydroxide is $+14.6$ Cal. for the first equivalent, and $+13.8$ Cal. for the second equivalent, a result similar to those obtained by Cavalier with methyl- and ethyl-phosphoric acids, and by the author with ethylphosphoric acid and glycerol-

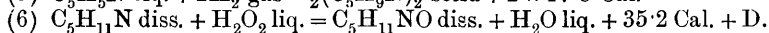
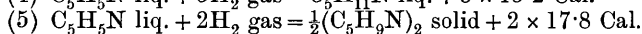
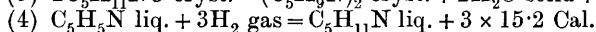
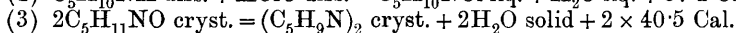
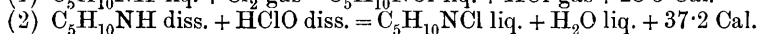
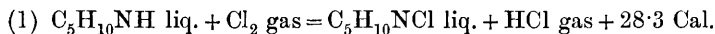
phosphoric acid. Phenylphosphoric acid also behaves in the same way as the others with methyl-orange and phenolphthalein.

When phosphoric anhydride acts on an alcohol or a phenol, solid metaphosphoric acid and a syrupy liquid are obtained. If some of the liquid is dissolved in water, the quantity of alkali necessary to make it neutral to methyl-orange is higher than that required to pass from neutrality toward methyl-orange to neutrality toward phenolphthalein. The syrupy liquid contains no metaphosphoric acid, and hence the effect just described must be due to the di-substituted phosphoric acid that is present.

C. H. B.

Pyridine Bases. By MARCEL DELÉPINE (*Compt. rend.*, 1898, 126, 1794—1797).—The following thermochemical data were determined.

	Pyridine.	Piperidine.
Specific heat (between 16° and 96—98°) ...	33·5 Cal.	44·1 Cal.
Heat of volatilisation.....	8·57 „	7·9 „
Heat of combustion at constant volume (liquid).....	664·68 „	825·21 „
Heat of combustion at constant pressure (liquid).....	665·1 „	826·5 „
Heat of combustion at constant pressure (gas).....	673·7 „	834·4 „
Heat of formation (liquid).....	-21·1 „	+24·5 „
„ „ (gas)	-29·7 „	+16·6 „
	Chloropiperidine.	Dipiperidine.
Heat of combustion at constant volume ...	789·6 Cal.	2 × 766·37 Cal.
Heat of combustion at constant pressure...	790·6 „	2 × 767·4 „
Heat of formation ...	+30·8 „	+2 × 14·6 „
		δ-Amido- valeraldehyde.
		805·55 Cal.
		806·55 „
		+44·45 „



D being the heat of dissolution of δ-amidovaleraldehyde.

The value 28·3 Cal. given by equation (1) is in fair accordance with the mean value for the heat of substitution of chlorine in organic compounds. Equation (2) explains the fact that piperidine displaces the alkalis from hypochlorites, the latter being formed from hypochlorous acid with the evolution of at most 10 Cal. From the value given by equation (3) should be deducted the unknown heat of polymerisation of $2C_5H_9N$ into $(C_5H_9N)_2$. Supposing this to be equal to the heat of polymerisation of amylene into diamylene (11·8 Cal.), there still remains a large development of heat in equation (3) analogous to that noticed in the quinoline series.

The chloropiperidine employed in these experiments was obtained by the action of concentrated alkali hypochlorite solution on piperi-

dine; it had a sp. gr. = 1.0667 at $0^{\circ}/4^{\circ}$ and 1.0517 at $17^{\circ}/4^{\circ}$, and boiled at 58° under 39 mm. pressure and 55° under 30 mm. pressure. By the action of sodium hypobromite on piperidine, bromopiperidine is obtained, in theoretical quantity, as a heavy, yellow oil of powerful odour. It is much more unstable than the chloro-derivative, and deflagrates spontaneously on keeping; hence it may, perhaps, be regarded as an alkylamide derived from hypobromous acid and not as a simple bromine substitution derivative. N. L.

The Differential Areometer as Areo-Pyknometer for Determining the Sp. Gr. of Powders. By PAUL FUCHS (*Zeit. angew. Chem.*, 1898, 623—625).—This is a patented instrument resembling the ordinary hydrometer, but so arranged that the bottom of the bulb is fitted with an inverted stoppered tube resembling a weighing tube, which can be removed at pleasure. In water, the instrument will sink to the zero division, which is at the bottom of the stem.

The stoppered tube has a mark representing 2 c.c., and must be filled up to that mark with the finely powdered substance such as cement, this being gently pressed in by means of a metallic disc attached to a rod. If the instrument now sinks down to, say, 1.8, this will be the specific gravity of the substance. The whole operation takes about 5 minutes, and the results are technically accurate. L. DE K.

Tables for the Correction of Errors caused by Variation in Temperature when using the "Procentareometer." By PAUL FUCHS (*Zeit. angew. Chem.*, 1898, 745—755).—These are tables very useful to those who employ "Gustav Müller's areometer" for estimating the percentage of nitric, sulphuric, and hydrochloric acids, and the strength of ammonia. L. DE K.

Temperature-Correction Tables for Specific Gravity Determinations. By PAUL FUCHS (*Zeit. angew. Chem.*, 1898, 909—914).—The author (compare preceding abstract) gives similar specific gravity tables for ethylic acetate, acetone, ether, ethylbenzene, formic acid, amylic acetate, aniline, benzene, chloroform, glycerol, methylic alcohol, nitrobenzene, petroleum, turpentine, toluene, xylene, solutions of potassium chloride and nitrate, sodium chloride, nitrate, and sulphate, ammonium chloride and carbonate, and calcium chloride. L. DE K.

Eutropic Series of the Calcium Group. By A. EPPLER (*Zeit. Kryst. Min.*, 1898, 30, 118—175).—The term catametric eutropy, or, shortly, eutropy, has been introduced by G. Linck (*Zeit. physikal. Chem.*, 1896, 19, 193) for those special cases of isomorphism in which the geometrical and physical characters of members of a series regularly increase or decrease with increase of atomic weight of the varying element, as, for example, in Tutton's potassium, rubidium, and caesium compounds. In a later paper (*Zeit. Kryst. Min.*, 1896, 26, 281), Linck states that the quotients of the crystal volume by the molecular volume of the different members of such a series are in the ratio of simple rational numbers. The first relation has been partly tested by Orloff (*Abstr.*, 1896, ii, 355), and the present author finds that both hold good in the calcium-strontium-barium group, with, however, one or two

exceptions, as in the anhydrous sulphates, anhydrite, celestite, and barytes.

Numerous data concerning the crystallised compounds of calcium, strontium, and barium are brought together and compared, and several new geometrical, optical, and density determinations are given. For cubic crystals, the crystal volume becomes unity, and the above quotient is inversely proportional to the molecular volume. In the cubic oxides, fluorides, chlorides, and nitrates of calcium, strontium, and barium, the ratios are 11:15:19, 14:17:20, 18:19:20, 20:21:22 respectively, thus decreasing with the increase in the total molecular weight. Lead compounds, although often isomorphous with those of calcium, &c., do not belong to the same eutropic series, since the physical constants sometimes fall between those of calcium and strontium, or before or after those of the corresponding barium salt.

L. J. S.

Dissociation of Hydrogen Selenide. By H. PÉLABON (*Zeit. physikal. Chem.*, 1898, 26, 659—689).—The main results given in this paper have already appeared (Abstr., 1896, ii, 96; 1897, ii, 251).

A Diffusion Apparatus. By MAX A. SIEGFRIED (*Ber.*, 1898, 31, 1825—1826).—This consists of a cylindrical glass ring and two cylindrical glass jars, with their axes horizontal. The two rims of the jars and both rims of the ring are welted and ground, and by means of screw clamps attached to metal collars the ground glass surfaces can be pressed together, a piece of parchment paper being first placed at each junction, and made water-tight by means of india-rubber rings or washers. The whole thus consists of a closed cylinder, lying horizontally, and divided into three compartments by diaphragms of parchment paper. The central vessel contains the liquid to be dialysed; this is stirred by a stirrer which passes through a tubulus on the top of the vessel, and is driven by a small turbine. The two end vessels have each two tubuli, one on the top, the other at the side; into one vessel, through the top tubulus, flows the waste water from the turbine; it passes out at the side tubulus, and along glass and indiarubber tubing to the second vessel, which it enters through the side tubulus, and leaves through a glass tube inserted in the top tubulus. The apparatus is manufactured by Franz Hugershoff of Leipsic in three sizes; in the largest size, the central vessel has a capacity of about $2\frac{1}{2}$ litres.

C. F. B.

Solid Solutions of Benzene in Phenol. By GIUSEPPE BRUNI (*Gazzetta*, 1898, 28, i, 249—258).—Beckmann pointed out (Abstr., 1897, ii, 362) that in cryoscopic determinations in which a solid solution of the solvent and dissolved substances separates, the molecular weight of the dissolved substance can be correctly ascertained from the equation $M_c = M(1 - a)$; M_c is the corrected molecular weight, M the molecular weight deduced from the freezing point, and a the coefficient of distribution of the dissolved substance between the solid and liquid solutions. Cryoscopic determinations with solutions of phenol in benzene as solvent, in which the concentration c increases from 1.2 to 7.9, give values for M increasing from 153—188, whilst

the values of M_c increase from 100 to 148; the latter values are comparable in magnitude with the values of M for phenol obtained by the boiling point method in benzene solution, and by the cryoscopic method in paraxylene solution. Bodländer (Abstr., 1897, ii, 133) noted that the lack of uniformity amongst Garelli's numbers (Abstr., 1897, i, 26) is possibly due to a difference of molecular weight of the material dissolved in the two solvents. The author agrees with this view, but considers that Bodländer's method of calculation is faulty.

Solutions of benzene in phenol as the solvent are also cryoscopically abnormal; as c increases from 0.20 to 4.08, M increases from 87.7 to 91.3. Experiments made by Bijlert's method, using benzil as the normal third substance, showed that solid solutions of benzene in phenol were formed, the value of α being 0.24 to 0.33 where α is the coefficient of distribution $\alpha = C_s/C_m$; C_m is the mean of the initial and final concentrations of benzene in the liquid solution, and C_s is the corresponding concentration in the solid solution. The variation in the value of α is attributable to experimental error.

W. J. P.

Solid Solutions of Pyridine and Piperidine in Benzene. By GIUSEPPE BRUNI (*Gazzetta*, 1898, 28, i, 259—268).—The molecular weights of pyridine and piperidine determined in benzene solution by the cryoscopic method are always greater than the normal, but diminish as the concentration increases to $c =$ about 1, and after that increase as c increases; the values obtained agree on the whole with those obtained by Paternò. Applying Bijlert's method to solutions of piperidine in benzene, benzil being the third substance as before (compare preceding abstract), it was found that solid solutions of the base in the hydrocarbon were formed; the values of α , as the concentration increased, first fell and then rose in much the same way as the molecular weights. Using the Beckmann correction formula, values of M_c varying from 81.7 to 84.8 were obtained; these values are sufficiently close to the normal value of 85.

W. J. P.

Solid Solutions of Open Chain Compounds. By GIUSEPPE BRUNI (*Gazzetta*, 1898, 28, i, 277—283).—Although solutions of closed chain compounds in closed chain solvents, namely, dihydronaphthalene in naphthalene, tetrahydrodiphenyl in diphenyl, and maleic anhydride in succinic anhydride, yield solid solutions, the same kind of behaviour is not observed amongst open chain compounds; oleic and butyric acids show normal cryoscopic behaviour, using stearic and crotonic acids respectively as solvents. This, as Garelli has remarked (Abstr., 1895, ii, 206), is probably due to the alteration of molecular symmetry being greater amongst open than amongst closed chain compounds.

Examples of solid solutions amongst open chain compounds must be sought amongst substances of similar molecular configuration. Trichloracetamide and tribromacetamide form solid solutions (Küster, Abstr., 1892, 396), so also do carbon tetrachloride and carbon tetrabromide (Rothmund, Abstr., 1898, i, 158).

Solutions of chloroform or iodoform in bromoform do not deposit the pure solvent on cooling, the value of M being approximately 600 instead of 394 for solutions of iodoform in bromoform in which c varies

from 0.22 to 3.49. Using Bijlert's method, with diphenyl as the third substance, the distribution coefficient a is found to be 0.35—0.37; on correcting by Beckmann's formula, $M_c = M(1 - a)$, the values of $M_c = 384$ to 392 are obtained.

Similarly, solid solutions are deposited on cooling solutions of ethylenic di-iodide or dichloride in ethylenic dibromide. The molecular weights of the dissolved substances are found as 430—443 or 121—132 respectively, instead of having the normal values of 280 or 99.

W. J. P.

Solubility of Carvoxime. By HEINRICH GOLDSCHMIDT and HERMON C. COOPER (*Zeit. physikal. Chem.*, 1898, **26**, 711—718).—Van't Hoff had suggested that two active modifications which are equally soluble in ordinary solvents might be found to have different solubilities in a solvent which is itself optically active, but experiments by Tolloczko (*Abstr.*, 1896, ii, 636) indicated that this was not the case. The authors therefore further investigated the question, and determined the solubility of dextro- and lævo-carvoxime in dextro-limonene. The + compound was prepared from + carvol and the - compound from + limonene nitrosylchloride; both melted at 72°, and gave rotations of +116.1° and -116.3° respectively. No difference of solubility in the + limonene could be detected. The solubility of the solid inactive carvoxime was found to differ from that of the dextro-compound, but there is no difference if the compounds are melted so that the inactive compound in the liquid state is but a mechanical mixture of the two active components; rapid crystallisation or solidification of the inactive compound also produces a mechanical mixture of the two modifications.

L. M. J.

Salt Formation in Alcoholic Solution. By SIMEON M. TANATAR and BORIS KLIMENKO (*Zeit. physikal. Chem.*, 1898, **27**, 172—174).—In alcoholic solutions, the heat of neutralisation of a strong acid or alkali is not the heat of formation of water from its ions owing to the slight dissociation of the compounds, whilst for ammonia no water results from the neutralisation. The heat of neutralisation of benzoic acid by potassium hydroxide was found to be 6.847 cal., and by ammonia 12.643, whilst the corresponding values in the case of lactic acid were 7.180 and 14.031. In aqueous solution, the heat of neutralisation of benzoic acid by potassium hydroxide is 13.4 cal., an equal value being obtained for lactic acid and sodium hydroxide. The following values for the heat of dissolution were also obtained; benzoic acid, -3.168; potassium benzoate, -3.213; ammonium benzoate, -1.779 cal.

L. M. J.

Crystalline Liquids. II. By RUDOLF SCHENCK (*Zeit. physikal. Chem.*, 1898, **27**, 167—171. Compare this vol., ii, 286).—Crystalline liquids are generally regarded as crystals, the internal friction of which is very small, and the author therefore determined the viscosity of some crystalline liquids and compared it with that of the same compounds in the isotropic state. The compounds examined were cholesteryl benzoate and paraoxyanisole (this vol., ii, 286), and the viscosity relative to that of benzene was determined. For the first

named compounds, determinations were made at 153.3° , 169.2° (crystalline), 180° , and 216° (isotropic), and it is seen that, at the transition temperature, there is a marked drop in the viscosity of the crystalline variety. The case of the parazoxyanisole is different, the viscosity of the crystalline modification being considerably less than that of the isotropic form. L. M. J.

Application of the Equilibrium Law to the Formation of Oceanic Salt Deposits, with Especial Reference to the Stassfurt Beds. By JACOBUS H. VAN'T HOFF and WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1898, 27, 75—93).—In order to deduce theoretically the order of deposition of salts in consequence of the evaporation of sea water, the relations of the individual salts present have to be first investigated, and the present paper deals with the solubility curves of the various hydrates of magnesium chloride, at temperatures from -33.6° to $+186^{\circ}$, when evolution of hydrogen chloride commences. The complete equilibrium curve for the chloride and water may be divided into the following parts:—(1) Stable solution in equilibrium with ice, from 0° to 33.6° ; (2) stable solutions in equilibrium with the following hydrates, $\text{MgCl}_2 + 12\text{H}_2\text{O}$, from -33.6° to -16.8° ; $\text{MgCl}_2 + 8\text{H}_2\text{O}$, from -16.8° to -3.4° ; $\text{MgCl}_2 + 6\text{H}_2\text{O}$, from -3.4° to 116.67° ; $\text{MgCl}_2 + 4\text{H}_2\text{O}$, from 116.67° to 181° ; $\text{MgCl}_2 + 2\text{H}_2\text{O}$, above 181° or 182° ; (3) labile solution in equilibrium with $\text{MgCl}_2 + 8\text{H}_2\text{O}$ (β) from -17.4° to -9.6° . Labile continuations of the curves for the hexahydrate and the dodecahydrate can be obtained meeting at -30° , whilst similar continuations of the ice and octahydrate equilibrium curves cut at -50° . The dodecahydrate was previously unknown, and is best produced by cooling a solution, containing a little more water than is required for the crystals, to about -20° , and then inducing local overcooling by solid carbonic anhydride. The stable and labile octahydrates, also previously unknown, can be produced in a similar manner by cooling a solution of the composition $\text{MgCl}_2 + 11\text{H}_2\text{O}$. Once formed, the labile hydrate might remain unchanged for a whole day, but its production could not be depended on. The values found for the solubility of the hexahydrate were in general slightly lower than those of other observers, probably owing to more complete freedom from calcium chloride. For the solubility determinations at the highest temperatures, a special form of apparatus was employed, which is described in the paper with the aid of diagrams. L. M. J.

Equilibrium in the System, Water, Alcohol, and Ethylenic Cyanide. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1898, 27, 95—122).—Of these three pairs of liquids, two pairs, namely, alcohol-cyanide and water-cyanide, only form two liquid layers between the temperature limits of 13 — 31° , and 18.5 — 55.5° respectively, and this leads to some highly interesting cases of equilibrium. The equilibrium curve for water-ethylenic cyanide consists of three portions: (1) a portion, *ab*, from -1.2 to 18.5 where the solid cyanide is in equilibrium with the solution and the quantity dissolved increases with temperature; (2) the portion, *bdc*, where two liquid phases occur with the critical point of complete miscibility at 55.5° ; (3) the portion, *cs*, from $+18.5^{\circ}$ to 54.5° , where the solid cyanide is in equilibrium

with a liquid phase containing a high percentage of the cyanide. By the addition of alcohol, the temperature of the triple phase points, b , c , is reduced, and the curve, bdc , of two liquid phases becomes more and more flattened owing to the lowering of the temperature of complete miscibility. The region where separation into two layers occurs becomes more and more confined, and when the percentage of alcohol reaches 56.1 the points b , d , c , coalesce, and there is no region of two liquid phases. The alcohol-cyanide equilibrium curve is completely analogous, but the critical temperature is 31.1° , and is lowered by the addition of water, so that for 28.6 per cent. of water the two liquid phases region disappears. Hence separation into two layers only occurs with aqueous alcohol when the concentration of the alcohol is below 56.1 or above 71.4 per cent. From the solubility data, the equilibrium can be represented by a surface in an equilateral triangular prism where the long side is a temperature axis; on the faces of the prism are the equilibrium curves for each pair, and any section at right angles to the axis gives the isothermal for the triple equilibrium. A section passing through the cyanide edge of the prism and cutting the water-alcohol face gives the solubility curve of the cyanide in aqueous alcohol of the indicated composition, and it is hence seen that in 71.4 per cent. alcohol (which is approximately equimolecular) the solubility increases enormously with the temperature between 3° and 5.9° ; at the lower temperature, 100 grams of the aqueous alcohol dissolve 42.3 grams of ethylenic cyanide, and at the higher temperature 305.5 grams. The isotherms are also interesting; in some cases, a line through the alcohol apex cuts the curve in three points, here, therefore, the effect of the addition of alcohol to the other components is to cause (1) dissolution of cyanide and production of homogeneous solution; (2) deposition of cyanide; (3) dissolution of deposited cyanide and re-formation of homogeneous solution. At a temperature of 5° , it is seen that, whilst 100 grams of alcohol dissolve 7 grams of cyanide, and 100 grams of water dissolve 6 grams of cyanide, yet 100 grams of 71 per cent. alcohol dissolve 232 grams, so that the solubility in this mixture is thirty times as great as in either component. At this temperature also, the addition of alcohol leads to very complicated results, causing (1) dissolution of cyanide; (2) separation into two liquid phases, in equilibrium with solid cyanide; (3) two liquid phases; (4) a homogeneous solution; (5) separation into two liquid phases; (6) further deposition of solid cyanide; (7) disappearance of one liquid phase; (8) disappearance of solid and production of homogeneous solution. Other very interesting features of the equilibrium are noticed, but for most of them the equilibrium diagrams are necessary. (See also Abstr., this vol., ii, 329, 424; 1897, ii, 483.)

L. M. J.

Influence of Concentration on Reaction Velocities. By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1898, 26, 728—738).—The reaction studied was the oxidation of an acidified solution of potassium iodide, an action which is dependent on temperature, light intensity, and the nature and concentration of the added acid. The variation of the velocity with the concentration of the potassium iodide showed the reaction to be one of the second order. The effect of light

was found to be in the following order, white, yellow, green, red, and was independent of the acid employed. The effects of the different acids used gave the following order, hydrochloric acid, sulphuric acid, oxalic acid, acetic acid, and although this order is also that of the dissociation, yet the quantitative effects are not proportional to the dissociation. With acetic acid, the velocity of oxidation is at first proportional to the concentration of the acid, but at a concentration of about 50 per cent., the velocity increases enormously, reaches a maximum between 70 and 90 per cent., and again rapidly decreases. With sulphuric and hydrochloric acids also, the increase of velocity is far more rapid than the increase of concentration of the ions. It is worthy of note also that Spring and Aubel found that an increase of the velocity of dissolution of metals in acids occurred at a concentration of about 40 per cent. (Abstr., 1887, 1074). L. M. J.

Relative Velocity of Hydrolysis of Ethylic Salts of Normal Acids of the Oxalic Series. By EDVARD HJELT (*Ber.*, 1898, 31, 1844—1847).—The rate of hydrolysis (by soda) was determined at 17°, using N/20 solutions in 96 per cent. alcohol (Abstr., 1896, i, 205). The expression $x \div (A - x) \sqrt{t}$, has an approximately constant value, which is regarded as the constant of velocity of the hydrolysis. Side by side with the values of this are tabulated the values of the dissociation constants K_1 and K_2 , of the first and second hydrogen atoms of these acids, as determined by W. A. Smith (this vol., ii, 285). It will be seen that here, when there are no changes, such as the introduction of a methyl group, likely to have a stereochemical effect on the constant of velocity, the latter decreases with the dissociation constant of the first hydrogen atom, and is not dependent on that of the second hydrogen atom, as Smith supposed it might be.

Acid.	Velocity constant.	$10^6 \times K_1$.	$10^6 \times K_2$.
Malonic	0·224	1580	1·0
Succinic	0·088	66·5	2·3
Glutaric	0·073	47·3	2·7
Pimelic	0·058	32·3	2·6
Suberic	0·042	29·9	2·5
Azelaic	0·037	25·3	2·7
Sebacic	0·037	23·8	2·6

C. F. B.

Report of the Committee on Atomic Weights. By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1898, 20, 163—173).—A *résumé* of the work published during 1897 on the atomic weights of carbon, nitrogen, chlorine, silver, aluminium, nickel, cobalt, tungsten, and cerium; a corrected table of atomic weights of all the elements is appended. W. A. D.

Table of Atomic Weights. By THEODORE W. RICHARDS (*Amer. Chem. J.*, 1898, 20, 543—554).—The atomic weights of 74 elements are given, that of oxygen being taken as 16; the values are

compiled from the most recent data, and, with the exception of those of the seven elements, antimony (120.0), cadmium (112.3), calcium (40.0), magnesium (24.36), platinum (195.2), tungsten (184.4), and uranium (240.0), are the same as those given by Clarke ("Smithsonian Collection of Constants of Nature," 5, 1897). Reasons are given in detail for the choice made between the conflicting values for the atomic weights of the elements mentioned above. W. A. D.

Atomic Weight or Atomic Gravitation. By LUDWIG DULK (*Ber.*, 1898, 31, 1865—1876).—This paper appears to be an account of a book published by the author (*Atomgewicht oder Atomgravitation*, Trewendt, Breslau, 1898), but is so condensed that it is hardly intelligible in itself. "This study is based on the recognised necessity of ceasing to regard matter as homogeneous. The atoms are no longer regarded as composed of different amounts of one and the same matter; they are conceived as systems of geometrical points, or of ether-vortices rotating about fixed positions of equilibrium. These bring the cosmic ether, which is conceived as continuous, into motion, the faster the nearer they lie to one another. This motion is assumed to be inversely proportional to the square of the distance, in accordance with the behaviour of all known forces that act at a distance, and in this way the gravitation of the atom, apparent to us as its atomic weight, is calculated." The atomic weights are calculated by means of some such expression as $n/a^2(1 + b/2)$, in which the constants are determined by geometrical considerations; for example, a regular figure is taken with a number of sides (n) equal to the valency of the element, and such figures are arranged in a symmetrical system; the diameter of the circle circumscribing an individual figure being taken as unity, b is that of the circle circumscribing the system, and a is the length of the side of each figure. As another example of the methods employed, the atomic weight of copper may be quoted; this is calculated as

$$3 \cdot \frac{1}{(\frac{1}{3})^2} \left(1 + \frac{\sqrt{3}}{2}\right) + \frac{3}{2} \cdot \frac{1}{(\frac{1}{3})^4} \cdot \frac{1}{\left(\frac{2}{\frac{1}{3}} - 2\right)^2} \left(1 + \frac{1}{\sqrt{2}}\right) = 63.339.$$

In such ways as these, the following atomic weights are calculated :

Na = 23.06, K = 39.111, Rb = 84.96, Cs = 131.1, N = 14.0, O = 16.0, F = 18.928, B = 11.041, C = 11.9497, Si = 28.0, Cl = 35.464, Br = 79.666, I = 126.23, Cu = 63.339, Ag = 107.717, Au = 195.77, Hg = 198.45, Zn = 65.385, Cd = 112.0, Tl = 204.298.

The specific gravities of the elements, free or in combination, are also calculated by means of expressions of the form of either $x/a^2(\frac{1}{a} - 1)$ or Y/a^2 . For example, that of copper is

$$\frac{1}{(\frac{1}{3})^2} \cdot \frac{1}{3 - 1} \cdot 9 \cdot 0.220 = 8.93. \quad \text{C. F. B.}$$

The Periodic System and the Properties of Inorganic Compounds. By JAMES LOCKE (*Amer. Chem. J.*, 1898, 20, 581—592).—Although Mendeléeff's law is true as regards the physical and

chemical properties of the elements themselves, it is, in the author's opinion, inaccurate to say that the nature of the compounds of an element is a function of its atomic weight. From this point of view, the character of the so-called "typical" elements is discussed. Although lithium, beryllium, boron, and carbon, in the elementary state, are the strict homologues of the elements in the groups to which they belong, the compounds of beryllium are entirely different in character from those of any of the metals of the second group. Yet the compounds of the "typical" element lithium resemble in every respect those of the alkali metals; and the compounds of carbon those of silicon. Beryllium lies, as regards atomic weight, between lithium and carbon, so that its position as a typical element cannot be held to explain its anomalous character. Similarly, although fluorine as an element closely resembles the other halogens, many of its compounds differ from those of the latter in a very marked manner.

The proximity of cobalt and manganese to iron in the fourth series enables them to form well-defined double cyanides of the type $K_3MC_6N_6$, isomorphous with potassium ferricyanide; chromium and vanadium also (compare this vol., ii, 598), in the same series, form similar compounds, whilst the alums of the five elements named are isomorphous with those formed by titanium. The sesquioxide of scandium closely resembles that of titanium, yet all the other scandium compounds are similar to those of the rare earths. The proximity of scandium to titanium fails to confer on the tervalent compounds of the latter any single one of the properties of the rare earths.

W. A. D.

Cooling Pipette. By FRIEDRICHS (*Zeit. anal. Chem.*, 1898, 37, 443).—A pipette for taking up hot liquids. The lower tube is contracted into a spiral; the upper is fitted with a caoutchouc ball.

M. J. S.

Pipette with Closing Appliance. By CARL SANDER (*Zeit. anal. Chem.*, 1898, 37, 497).—The upper tube of the pipette is converted, by means of side apertures and a glass collar, into a kind of 3-way stop-cock by which communication is established either with a permanently connected aspirator or with the external air. A figure is given.

M. J. S.

Some New Forms of Apparatus. By AUGUSTUS E. KNORR (*J. Amer. Chem. Soc.*, 1897, 19, 817—820).—1. *An automatic filtering syphon.*—The longer limb of the syphon tube dips into the liquid in the funnel, and is closed by a ground conical glass valve, the lower part of which is blown out into a bulb, so that it rises with the level of the liquid and automatically stops the supply as soon as the funnel is full. The upper end of the valve stem bears a knob which, engaging with a constriction in the funnel tube, prevents the valve dropping out of the tube.

2. *A new form of gas generator.*—The solid substance required for the generation of the gas is placed in a calcium chloride tower, the acid being added from an acid funnel at the top. The novel feature of the apparatus is a U-shaped syphon tube inserted in the lower

opening of the tower, which is made of such a length that, while it allows the spent acid to flow away constantly, also acts as a hydraulic seal against the escape of gas.
A. H.

An Efficient Gas-pressure Regulator. By PAUL MURRILL (*J. Amer. Chem. Soc.*, 1898, 20, 501—504).—The apparatus, which is designed for use with a thermostat, consists of an inner and an outer vessel, the latter partially filled with water. The inner vessel, which can move freely up or down, is attached by means of a lever to the tap of the gas inlet tube; as gas enters, this vessel is lifted, at the same time closing the valve. If the outlets are closed, it rises until the valve is entirely closed, in which position it will remain; but when the exit tubes are opened, it falls, reopening the valve, admitting gas at the same rate at which it is consumed, and delivering it at a pressure which is measured by the weight of the inner vessel, *plus* or *minus* the resistance due to friction.

A. W. C.

New Form of Water Blast. By BERTRAM B. BOLTWOOD (*Amer. Chem. J.*, 1898, 20, 577—580).—A convenient form of apparatus is described for supplying relatively small volumes of air at low pressure; it is claimed to be nearly three times more efficient, as regards the volume of water consumed per cubic foot of air supplied, than the forms described by Muenke and by Richards. For the details of construction, the original must be consulted.
W. A. D.

Lecture Experiments with Liquid Air. By ALBERT LADENBURG (*Ber.*, 1898, 31, 1968—1969).—The following experiments can readily be performed before a class by the help of Linde's modified apparatus.

1. Carbonic anhydride, when passed into liquid air, is at once precipitated as a white, snow-like powder.
2. Mercury at once becomes solid, and retains this form for some time.
3. Alcohol is insoluble in liquid air, but solidifies in hard, crystalline drops, which may be heard to rattle against the glass when the containing vessel is shaken.
4. Ozone can readily be liquefied to a deep blue, oily liquid.
5. Acetylene is at once solidified and can be pressed into cylinders in the same way as solid carbonic anhydride.
6. When concentrated hydrochloric acid is cooled for a few minutes in liquid air and a piece of potassium then added, no action occurs, but after standing in the open air for a short time explosive action occurs.
7. When liquid air is poured into water, the light blue drops fall to the bottom, but are driven upwards by the gas formed round their surface, the liquid air being in the spheroidal state.

A. H.

Inorganic Chemistry.

Boiling Point of Liquid Ozone. By LOUIS TROOST (*Compt. rend.*, 1898, 126, 1751—1753).—Ozone was liquefied in a vertical tube immersed in a bath of liquid oxygen, and the latter was then lowered

until the readings of a galvanometer in circuit with a thermo-junction previously introduced into the tube were constant during the ebullition of the ozone. The boiling point of liquid ozone was thus found to be -119° at the atmospheric pressure. N. L.

Action of Potassium Permanganate and of Sodium Peroxide on the Acids of Sulphur and of Iodine. By ANTONIO LONGI and L. BONAVIA (*Gazzetta*, 1898, 28, i, 325—335).—The authors find that potassium permanganate, in alkaline solution, oxidises potassium sulphite, thiosulphate, trithionate, tetrathionate, sulphide, and polysulphide to potassium sulphate; potassium dithionate is not oxidised at all, and the oxidation of the tri- or tetra-thionate proceeds slowly. Potassium permanganate oxidises iodides quantitatively, in alkaline solutions containing not more than 0.05 gram per 100 c.c., in accordance with the equation $MI + Mn_2O_7 = MIO_3 + 2MnO_2$.

Sodium peroxide immediately and completely oxidises sulphites, thiosulphates, trithionates, tetrathionates, sulphides, and polysulphides, but acts very slowly on the dithionates; the peroxide has no action on iodates or iodides, but in very dilute solutions reacts with iodine forming iodide, whilst in more concentrated solutions the oxy-acids of iodine are produced. W. J. P.

Persulphates. By HUGH MARSHALL (*J. Soc. Chem. Ind.*, 1897, 16, 396—399).—A *résumé* of the results obtained by the author (*Trans.*, 1891, 771, and *Abstr.*, 1891, 982) and by Elbs and Schönherr (*Abstr.*, 1896, ii, 519). W. A. D.

Reduction of Thiosulphates to Sulphites in Alkaline Solution. By RUDOLPH F. WEINLAND and A. GUTMANN (*Zeit. anorg. Chem.*, 1898, 17, 409—421).—Sodium thiosulphate, when treated with sodium arsenite in concentrated solution, is reduced at the ordinary temperature with development of heat. The products are sodium monothio-oxyarsenate, $Na_3AsSO_3 + 12H_2O$, which crystallises out, and sodium sulphite, which remains in solution; a small quantity of arsenic is also precipitated. Potassium thiosulphate and potassium arsenite react in a similar manner, but the potassium monothio-oxyarsenate is obtained, after the sulphite has crystallised, on evaporating the mother liquors over sulphuric acid. A solution of calcium thiosulphate, when treated with sodium arsenite, yields a precipitate of calcium arsenite, and on heating the mixture, calcium monothio-oxyarsenate, calcium sulphite, and sodium monothio-oxyarsenate are formed.

Sodium hydrogen arsenite and sodium thiosulphate, when allowed to react at the ordinary temperature, yield sodium monothio-oxyarsenate, sodium sulphite, and a small quantity of arsenic. When, however, the mixture is heated, a yellowish-red product is obtained which does not contain thio-oxyarsenate. The corresponding potassium salts behave in a similar manner.

Sodium thiosulphate, when treated with sodium dihydrogen arsenite, is converted into sulphite; a considerable quantity of arsenic is precipitated, and then red arsenic bisulphide. The mother liquor from the sodium sulphite does not crystallise when allowed to evaporate over sulphuric acid, but when heated on the water bath it yields the thio-oxyarsenite, $Na_3As_{18}S_{24}O_7 + 30H_2O$.

Sodium thiosulphate, when heated with a concentrated solution of sodium antimonite, prepared from antimonyl sodium tartrate, in the proportions expressed by the formula $\text{COONa} \cdot \text{C}_5\text{H}_2(\text{OH})_2 \cdot \text{COOSbO} + 4\text{NaOH} + \text{Na}_2\text{S}_2\text{O}_3$, is reduced to sulphite, with the formation of sodium pyroantimonate and sodium thioantimonate. A similar mixture of the potassium salts, when heated, yields potassium antimonate and potassium thioantimonate. If, however, the mixture is allowed to remain at the ordinary temperature, antimony trisulphide is precipitated, and the mother liquor, when evaporated to a syrup, yields crystals which decompose on recrystallisation, and give a red precipitate of antimony sulphide on treating with ammonium chloride. The compound is, therefore, probably potassium dithio-oxyantimonate, $\text{K}_2\text{HSbS}_2\text{O}_2 + 2\text{H}_2\text{O}$.

Sodium thiosulphate yields a precipitate of stannous sulphide, with a solution of sodium stannite. If this precipitate is separated by filtration, the mother liquor contains sodium stannate and sodium sulphite. If, however, the stannous sulphide is allowed to remain in the mother liquor, it slowly dissolves, and on concentrating, sodium stannate and sodium sulphite crystallise out, and then sodium thio-stannate, $\text{Na}_4\text{SnS}_4 + 12\text{H}_2\text{O}$; the latter separates in beautiful, colourless to pale yellow crystals belonging to the monoclinic system; $a:b:c = 0.90304:1:0.36520$; $\beta = 92^\circ 5'$. Potassium stannate and thiosulphate behave in a similar manner to the sodium salts. *Potassium thio-stannate*, $\text{K}_4\text{SnS}_4 + 4\text{H}_2\text{O}$, which is precipitated from the final mother liquors by alcohol, crystallises in long, microscopic, white needles.

Sodium thiosulphate is without action on sodium plumbite at the ordinary temperature; and when heated on the water bath only a small quantity of lead sulphide and lead oxide are formed, the mother liquor containing most of the thiosulphate unaltered.

Phosphites, hypophosphites, and nitrites do not reduce thiosulphates either at the ordinary temperature or on boiling. A violent explosion takes place when a small quantity of a solution of sodium nitrite and sodium thiosulphate is evaporated to dryness, and then gently heated.

E. C. R.

Action of Sulphur Monochloride on Minerals. By EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1898, 20, 289—293).—Stibnite and chalcocite dissolve in sulphur monochloride with great development of heat, antimony and cupric chlorides being produced respectively; artificially prepared arsenic trisulphide behaves similarly. Although a great rise in temperature occurs when arsenopyrite, chalcopyrite, cinnabarite, and tetrahedrite are brought into contact with sulphur monochloride, the minerals are only completely decomposed on heating to 140° ; in each case, the corresponding metallic chloride is produced. Marcasite and pyrites are not acted on in the cold, although completely decomposed when heated at 140° ; linnæite millerite, gersdorffite, and rammelsbergite have to be heated to 170° , and cobaltite, smaltite, and ullmannite to 180° , with sulphur monochloride, before decomposition is complete. Sphalerite and galenite are more resistant, but are completely dissolved on heating to 250° , whilst a temperature of

300° is necessary in the case of molybdenite. On heating the oxides of molybdenum, tungsten, tantalum, and columbium, as well as the minerals, wolframite, scheelite, and columbite, with sulphur monochloride, all were dissolved, and from the solutions obtained, beautiful crystals separated on cooling. It appears that, in the latter cases, sulphur monochloride acts as an oxidising as well as a chlorinating agent; this behaviour is also especially noticeable in the case of marcasite and chalcocite, which give rise to ferric and cupric chlorides respectively.

W. A. D.

Atomic Weight of Tellurium. By RENÉ METZNER (*Compt. rend.*, 1898, 126, 1716—1719).—The atomic weight of tellurium was determined by converting the element into the sulphate by the action of sulphuric acid, and also by reducing tellurous anhydride, in presence of metallic silver, by carbonic oxide. The tellurium employed was obtained in a very pure and crystalline condition by the decomposition of hydrogen telluride by heat, as recommended by Ditte, whilst the tellurous anhydride was prepared by heating to fusion, with exclusion of air, the product of the action of water on tellurium tetrachloride. The results obtained by the two different methods are in close agreement, the extreme values being 127·8 (mean of 3 determinations) and 128·24 (mean of 4 determinations), and the mean value 127·9 (standard not stated); these numbers are higher than those found by Brauner and by Staudenmaier.

N. L.

Atomic Weight of Nitrogen. By MAURICE VÈZES (*Compt. rend.*, 1898, 126, 1714—1716).—The difference between the value for the atomic weight of nitrogen, calculated from physical data (14·005), and that based on chemical analysis (14·044) is attributed by Berthelot and Leduc to the presence of dissolved oxygen in the metallic silver used by Stas in his determinations, a source of error to which attention was first directed by Dumas. The author points out that Stas himself, in a posthumous memoir, showed that the silver employed by him contained not more than $\frac{1}{35500}$ of its weight of oxygen, an amount too small to affect sensibly the atomic weights concerned. Applying the correction corresponding with this result, the atomic weight of nitrogen becomes 14·040, a number differing but little from the uncorrected value, but appreciably higher than that found by Berthelot and by Leduc.

N. L.

The Reaction between Phosphorus and Nitric Acid. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1898, 28, i, 397—402).—Personne (*Bull. soc. chim.*, 1864, 163) and Maumené (*Ann. chim. phys.*, 1864, [iv], 3, 319) have shown that ammonia is formed during the action of nitric acid on phosphorus. The author finds on exposing red phosphorus to the action of excess of 17·3, 28·3, and 68 per cent. nitric acid at 13—14° until all is dissolved, that 1 gram of phosphorus causes the production of 0·0739, 0·0824, and 0·0095 gram of ammonia respectively as the mean of four experiments with each concentration of acid. The results of the individual experiments differ considerably, and the time required for solution of the phosphorus also varies.

W. J. P.

Action of Sodammonium in Excess on Red Phosphorus. By C. HUGOT (*Compt. rend.*, 1898, 126, 1719—1722. Compare Abstr., 1896, ii, 20).—When a mixture of weighed amounts of red phosphorus and sodium is left in contact with liquid ammonia, a yellow, crystalline substance of the formula $P_2H_3Na_3$ is produced, hydrogen phosphide and sodamide being simultaneously formed. This compound is decomposed by acids and by water, with liberation of hydrogen phosphide; and when heated in a vacuum above 100° , loses hydrogen phosphide and hydrogen. An excess of sodium must be employed in its preparation, otherwise sodium phosphamide, PH_2Na , and other compounds are also produced. N. L.

Existence of Orthosilicic Acid. By THOMAS H. NORTON and D. M. ROTH (*J. Amer. Chem. Soc.*, 1897, 19, 832—835).—The substance obtained by washing precipitated silicic acid, prepared from silicon fluoride, with benzene or absolute ether, and then rapidly pressing the product between sheets of bibulous paper, has the composition required by the formula H_4SiO_4 . It is an amorphous, white powder which loses its water steadily on exposure to the air, especially when in contact with absorbent media. Thus if the pressing between filter papers be continued after the ether has been removed, rapid loss of water takes place, as much as 10 per cent. of the total water being in some cases lost in 5 minutes. Absolute alcohol cannot be used instead of ether, as it causes rapid dehydration. The authors consider that these experiments establish the existence of orthosilicic acid as a definite compound. A. H.

Carbonic Anhydride in the Atmosphere. By ALBERT LÉVY and H. HENRIET (*Compt. rend.*, 1898, 126, 1651—1653).—The error which, as shown by Gautier (this vol., ii, 641), arises from the use of potash instead of baryta as an absorbent for carbonic anhydride, is too small to sensibly affect the results of the daily observations carried out by the authors during the last twenty years. A series of duplicate estimations with both absorbents show that in the neighbourhood of the country the results obtained by the use of potash and of baryta are identical; in the centre of the town, however, baryta often gives higher results than potash, the difference amounting sometimes only to one-millionth of the volume of air employed, and sometimes to thirty times this amount. In the latter case, however, it is found that the same results are obtained with potash as with baryta if the air is left in contact with the alkali for a sufficiently long time. This fact, together with the results of other experiments to be described hereafter, induce the authors to believe that the alkalis not only absorb the carbonic anhydride actually present in the air, but also, and with different rapidity, facilitate the oxidation of the carbon contained in the organic matter existing in the atmosphere. The existence of such organic matter is proved by the fact that if a sample of air, giving different results with potash and baryta, is passed over heated cupric oxide and the carbonic anhydride again determined, identical results, slightly higher than before, are obtained with the two alkalis. Experiments made with air at the level of the soil tend to show that the earth is the principal source of these gaseous organic substances, and

that the latter are, in the country, oxidised by atmospheric ozone. It is also suggested that the relatively large proportion of carbonic anhydride present in fogs, as well as the odour of the latter, are closely connected with the existence of gaseous organic compounds, and with phenomena of condensation brought about by sudden alterations of pressure. N. L.

Limits of Inflammability of Carbonic Oxide. By HENRI LE CHATELIER and O. BOUDOUARD (*Compt. rend.*, 1898, 126, 1344—1347).—Mixtures of carbonic oxide and air are explosive when containing from 15.9 to 74.5 per cent. of the combustible gas, the experiments being carried out in a tube of 40 mm. diameter. If narrow tubes be employed, the limits of inflammability approach each other, and for tubes of less than 2.3 mm. diameter there is no explosive mixture. The inflammability diminishes rapidly with the pressure, and increases with rise of temperature. Mixtures of carbonic oxide and acetylene with air are found to obey the relation, previously found to hold for mixtures of methane and coal-gas, $\frac{n}{N} + \frac{n^1}{N^1} = 1$ where n and n^1 are the lower limits of inflammability of the mixtures, and N and N^1 are the limits for each of the two combustible gases when separately mixed with air. This relation is found to hold only approximately for mixtures of carbonic oxide and hydrogen with air. N. L.

Limits of Inflammability of Combustible Vapours. By HENRI LE CHATELIER and O. BOUDOUARD (*Compt. rend.*, 1898, 126, 1510—1513, —The authors have determined the limit of inflammability of the vapours of a large number of carbon compounds, and find that, except in the case of carbon bisulphide, the molecular heat of combustion of the limiting mixture lies between 9 Cal. and 13 Cal., and in most cases is between 12 Cal. and 13 Cal. The quantity of oxygen consumed in the combustion of these mixtures also varies but little, and is about 11.5 per cent. of the total volume. C. H. B.

New Atmospheric Gases. By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Compt. rend.*, 1898, 126, 1762—1763).—Two new gases, for which the names *neon* and *metargon* are proposed, were obtained by the fractional distillation of liquid argon. The first fractions consisted of neon, the spectrum of which is characterised by a large number of strong lines in the orange-red and yellow, and some lines in the deep violet. Towards the end of the distillation, a solid substance was formed which volatilised very slowly and could therefore be obtained in a high state of purity. This gas, metargon, has a density (19.87) almost equal to that of argon (19.94), but its spectrum is quite different. Among the numerous lines which it exhibits, there is one in the green occupying a position not yet recognised and one in the yellow at $\lambda 5849.6$. The latter is not coincident with the similar lines of krypton and helium, which are at $\lambda 5866.5$ and $\lambda 5875.9$ respectively. Both neon and metargon are monatomic gases, the ratio of the two specific heats being in each case 1.66. The intermediate fractions obtained in the distillation of liquid argon are still under examination. N. L.

Action of Sulphur on Sodium. By JAMES LOCKE and ALFRED AUSTELL (*Amer. Chem. J.*, 1898, 20, 592—594).—Quantities of sulphur corresponding with the compounds Na_2S , Na_2S_2 , Na_2S_3 , Na_2S_4 , and Na_2S_5 , were dissolved in hot toluene, and added to sodium covered with the same solvent at its boiling temperature; until the amount of sulphur was sufficient to form the compound Na_2S_3 , a considerable quantity of sodium remained unacted on. Products of practically the same composition (28.89 and 28.57 per cent. of sodium respectively) were obtained in the two cases where the quantities were those required to form Na_2S_3 and Na_2S_4 ; both products probably consisted of a mixture of these two substances.

From the above results, it appears that sodium monosulphide is not formed by the direct combination of sodium and sulphur at the temperature of boiling toluene; the same result was obtained at the temperature of boiling naphthalene (218°). W. A. D.

Ammonium Selenide. By VICTOR LENHER and EDGAR FRANCIS SMITH (*J. Amer. Chem. Soc.*, 1898, 20, 277—278).—On saturating with hydrogen selenide a solution of 5 grams of ammonium molybdate in 50 c.c. of water to which 20 c.c. of strongest aqueous ammonia had been added, a dark red solution was obtained, from which, on evaporation black, anhydrous, orthorhombic prisms of ammonium selenide separated. The crystalline product was stable in the air, and dissolved in water to a dark red solution which gave a precipitate of selenides from neutral or alkaline solutions of metallic salts; the solution, however, gradually decomposed on exposure to the air, selenium being precipitated.

The selenium was determined in the crystalline salt by a method communicated by H. F. Keller. A weighed quantity of the substance was dissolved in very dilute caustic soda, and an excess of hydroxylamine hydrochloride added; on boiling the solution for several minutes, selenium was precipitated, which was collected, dried at 105°, and weighed.

It is noteworthy that only from ammoniacal molybdate solutions of the concentration given can the black crystals of ammonium selenide be obtained; under other conditions, selenium alone is formed.

W. A. D.

Some Reactions of Ammonium Salts. By WATSON SMITH (*J. Soc. Chem. Ind.*, 1895, 14, 629—631).—Nearly pure ammonium hydrogen sulphate can be prepared by heating the normal sulphate initially at 300—320° in a platinum dish, and finally almost to dull redness. Nitrogen is not liberated from ammonium hydrogen sulphate at temperatures up to 360°, but is rapidly evolved at 450°, when the residue contains a considerable quantity of ammonium sulphite. On heating finely powdered ammonium sulphate at 160°, ammonia is rapidly evolved, ammonium hydrogen sulphate being formed; if, however, gaseous ammonia is passed through the latter in the fused state at 310—320°, it is absorbed until 70 per cent. of the salt is converted into normal ammonium sulphate; at 350—360°, however, 46.8 per cent., and at 410—420°, 85.6 per cent., of the ammonium

hydrogen sulphate remains unacted on. If a slow current of gaseous ammonia is passed through the fused salt at 420° , a partial reduction to sulphite takes place, and nitrogen is liberated. If, in any of the above experiments a stream of air be substituted for the ammonia after the limit of absorption of the latter has been reached, ammonia is rapidly evolved, even at temperatures considerably below those at which the absorption took place.

In the light of the above results, the author discusses Hodgkinson and Bellairs' observations (Proc., 1895, 114) on the action of metals on fused ammonium sulphate. It is pointed out that ammonium sulphate as such does not melt, but that when heated it is converted into ammonium hydrogen sulphate, with loss of ammonia; if, therefore, the normal salt were employed in the experiments cited, the evolution of ammonia at 160° cannot be attributed to the action of the metals on the salt, but simply to the spontaneous decomposition of the latter; ammonium hydrogen sulphate, however, melts at 146° , but is only decomposed at a temperature considerably above 160° , so that if this were employed, the ammonia evolved must be considered due to the action of the metals. That little hydrogen was obtained is explained by its reducing action in the nascent state on the sulphate, ammonium sulphite being produced. As regards the action of metals on fused ammonium nitrate, Velej has shown (*Phil. Trans.*, 1888, 257) that the latter dissociates into ammonia and nitric acid at a temperature somewhat below that "at which it undergoes resolution"; the results obtained by Hodgkinson and Bellairs were, therefore, probably due to the action of this nitric acid on the metals employed, and not to the direct interaction of the latter with the salt. W. A. D.

Comparative Affinities in the Case of Certain Salts of Ammonium and Sodium. By WATSON SMITH (*J. Soc. Chem. Ind.*, 1896, 15, 3—8. Compare preceding abstract).—On passing steam through ammonium sulphate at 270 — 310° , ammonia is at first rapidly evolved, although the evolution becomes slower as the quantity of ammonium hydrogen sulphate formed increases; no sulphurous acid is liberated. When ammonium sulphate is heated in a current of moist air, ammonia begins to be evolved at temperatures varying from 105° to 177° , according to the physical condition of the salt; on heating neutral solutions of the salt, ammonia begins to be given off perceptibly at 60° , and, on boiling, the solution gradually becomes acid.

99.1 per cent. of the ammonia theoretically lost in the conversion of ammonium sulphate into ammonium hydrogen sulphate is evolved on heating the dry salt at 300° during 8 hours, and rapidly removing the gases formed by means of an aspirator. Under these conditions, 0.146 per cent. only of the sulphuric anhydride is liberated as sulphurous anhydride. When, however, ammonium hydrogen sulphate is heated in a bulb freed from air at 300 — 350° , large quantities of sulphurous anhydride are evolved, whilst the residue consists almost entirely of sulphite; as, however, practically no nitrogen is formed, it is doubtful whether the reduction takes place according to the equation $3\text{NH}_4\text{HSO}_4 = \text{N}_2 + \text{NH}_4\text{HSO}_3 + 5\text{H}_2\text{O} + 2\text{SO}_2$. The fact that no am-

monia is evolved when ammonium sulphate is heated with concentrated sulphuric acid at 300° , is in accord with the known accuracy of Kjeldahl's method of estimating nitrogen.

When ammonium hydrogen sulphate is fused with oxalic acid, the latter is immediately decomposed into carbonic oxide and anhydride. A peculiar series of changes takes place when ammonium chloride is heated with an equivalent quantity of ammonium sulphate, either in the dry state or in solution. In both cases, ammonia is first evolved with the production of ammonium hydrogen sulphate; after a time, however, this interacts with the ammonium chloride, ammonium sulphate being formed, whilst hydrogen chloride is evolved. As the amount of normal sulphate formed increases, a condition of equilibrium is reached, at which hydrogen chloride ceases to be liberated, and the sulphate begins to decompose with evolution of ammonia. The above cycle of changes is repeated as long as the saline mixture is heated. When ammonium chloride is heated with ammonium hydrogen sulphate, hydrogen chloride is initially evolved; after a time, however, the ammonium sulphate formed decomposes, and regenerates ammonium hydrogen sulphate with loss of ammonia, so that the action is not continuous. In order to completely decompose the chloride, a large excess of the acid sulphate is necessary; under these circumstances, the ammonium sulphate formed is decomposed only with very great difficulty.

Corresponding to the above, on adding common salt to fused ammonium hydrogen sulphate, hydrogen chloride is evolved, and sodium ammonium sulphate formed; the reaction is, however, incomplete, and a small quantity of sulphite is formed. On further heating, ammonia is evolved and sodium hydrogen sulphate produced.

When ammonium chloride is heated with ammonium hydrogen sulphate and an excess of manganese dioxide, nearly 15 per cent. of its chlorine is evolved; sodium chloride, under similar conditions, yields about 20 per cent. of chlorine, whilst from a mixture of ammonium chloride (1 equiv.), sodium hydrogen sulphate (4 equivs.), manganese dioxide (4 equivs.), and a little water, as much as 83 per cent. of the combined chlorine was obtained, sodium ammonium sulphate being formed. This appears to crystallise with $3\text{H}_2\text{O}$, and not with $2\text{H}_2\text{O}$ as usually stated, and on being heated evolves ammonia perceptibly at 78° ; during 13 hours at $300\text{--}305^{\circ}$, 66.57 per cent. of the ammonia is evolved, but no sulphurous anhydride is formed. At 450° , a further quantity (7.7 per cent.) of ammonia is given off, but slight reduction to sulphite also takes place. The remaining portion of the ammonia appears to be more firmly retained by sodium hydrogen sulphate, in presence of an excess of the latter, than by ammonium sulphate, when a corresponding excess of ammonium hydrogen sulphate is present.

W. A. D.

Structural Isomerism in Inorganic Compounds. By ALEXANDER P. SABANÉEFF (*Zeit. anorg. Chem.*, 1898, 17, 480—493).—The author describes seven pairs, and a series of three metameric inorganic compounds. The first pair, hydroxylamine hypophosphite and ammonium

dihydrogen phosphite, have already been described (Abstr., 1897, ii, 170).

Hydroxylamine dithionate, $(\text{NH}_3\text{O})_2\text{H}_2\text{S}_2\text{O}_6$, is obtained by the action of hydroxylamine sulphate on barium dithionate. When the solution is evaporated at the ordinary temperature, a crystalline mass is obtained, together with a few large crystals which are similar in appearance to ammonium nitrate; it is partially decomposed when heated on the water bath, and at 120° is converted into hydroxylamine sulphate and sulphurous anhydride. It is isomeric with ammonium persulphate $(\text{NH}_3)_2\text{H}_2\text{S}_2\text{O}_8$.

Hydrazine phosphite, $\text{N}_2\text{H}_4\text{H}_3\text{PO}_3$, obtained from barium phosphite and hydrazine sulphate, is very hygroscopic and melts at 36° . It is isomeric with ammonium hydrogen amidophosphate, which decomposes at 120° and melts at 305° .

Hydrazine hydrogen phosphite, $\text{N}_2\text{H}_4(\text{H}_3\text{PO}_3)_2$, obtained from hydrazine sulphate and barium hydrogen phosphite, melts at 82° without decomposition. It is isomeric with ammonium hypophosphate, $(\text{NH}_3)_2\text{H}_4\text{P}_2\text{O}_6$, which melts at 170° (Salzer, Abstr., 1879, 106; 1882, 461).

Hydrazine phosphate, $\text{N}_2\text{H}_4\text{H}_3\text{PO}_4$, obtained from hydrazine sulphate and barium phosphate, or by neutralising phosphoric acid with hydrazine hydrate, melts at 82° . It is isomeric with hydroxylamine amidophosphate, $\text{NH}_3\text{O}\cdot\text{NH}_2\text{PO}(\text{OH})_2$, which decomposes at 95° .

Acid hydrazine phosphate, $\text{N}_2\text{H}_4(\text{H}_3\text{PO}_4)_2$, obtained from the barium salt, $\text{Ba}(\text{H}_2\text{PO}_4)_2$, is isomeric with *hydroxylamine hypophosphate*, $(\text{NH}_3\text{O})_2\text{H}_4\text{P}_2\text{O}_6$, which melts and decomposes at 139° .

Hydrazine hypophosphate, $\text{N}_2\text{H}_4\text{H}_4\text{P}_2\text{O}_6$, obtained by neutralising hypophosphoric acid with hydrazine hydrate and then adding an equal quantity of hypophosphoric acid, is sparingly soluble in water and melts at 152° . It is isomeric with ammonium dimetaphosphate, $(\text{NH}_4\text{PO}_3)_2$, which, according to the cryoscopic results and the electric conductivity described by Tammann (*Zeit. physikal. Chem.*, 6, 122) has the above formula.

Ammonium hydroxylaminosulphonate, $\text{NH}(\text{OH})\cdot\text{SO}_3\text{NH}_4$, is obtained by boiling a solution of potassium hydroxylaminosulphonate (*Annalen*, 241, 187) for a few minutes, then adding an excess of barium chloride, and after filtration adding barium hydroxide, whereby barium hydroxylaminosulphonate is precipitated; finally the latter is decomposed with ammonium sulphate; it is a crystalline mass which decomposes if kept. It is isomeric with hydroxylamine amidosulphonate, $\text{NH}_3\text{OH}\cdot\text{NH}_2\text{SO}_3$, and also with hydrazine sulphate, $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$.

E. C. R.

Preparation of Crystallised Calcium. By HENRI MOISSAN (*Compt. rend.*, 1898, 126, 1753—1758).—The author has repeated much of the work of previous experimenters, and finds that none of the processes hitherto employed are capable of yielding metallic calcium in a pure state. The separation of the metal from its amalgam is impracticable, the residue left on distillation being always impure. In the electrolysis of fused mixtures of salts of calcium and the alkali metals, the latter are the first to be liberated and then take part in

the reaction. When calcium salts are reduced by metallic sodium, a mixture of the two metals is always obtained, a state of equilibrium being finally reached which depends on the temperature and the relative proportions of the salts employed. Heating in contact with hydrogen or nitrogen must be avoided in the preparation of calcium, since under these conditions the hydride, CaH_2 , or the nitride are formed. Either of the two following methods yields metallic calcium in a pure crystalline state.

1.—Coarsely powdered, anhydrous calcium iodide (600 grams) is heated to dull redness in a closed iron crucible with 240 grams of sodium in small pieces. The calcium formed dissolves in the excess of sodium, from which it crystallises, on cooling, in brilliant, white, hexagonal crystals, which remain undissolved when the contents of the crucible are broken up and treated with absolute alcohol. The crystals are washed with ether and dried at the ordinary temperature in a current of dry carbonic anhydride or hydrogen. The yield in this process is about 50 per cent.

2.—Calcium iodide is fused at a dull red heat and electrolysed between a negative electrode of pure nickel and a positive electrode consisting of a cylinder of graphite. The metal is obtained either in fused globules or in crystals similar to those already described. The study of this reaction will be continued.

The metal obtained by the first process was found, by analysis, to contain 99 per cent. of calcium. N. L.

Phosphorescent Mixtures containing Strontium Sulphide. By JOSÉ RODRIGUEZ MOURELO (*Compt. rend.*, 1898, 126, 1508—1510).—Further experiments with mixtures of strontium, barium, and calcium sulphides with one another and with indifferent substances lead to the conclusions that (1) at least 2·5 per cent. of the active substance must be present, and beyond this limit the phosphorescence increases with the proportion of the active substance; (2) a longer exposure to diffused light is necessary when indifferent substances are present; (3) the intensity of the phosphorescence is greatly increased by the addition of small quantities of sodium carbonate and chloride and bismuth subnitrate to the mixture from which the sulphide is prepared; (4) the colour of the phosphorescence is always the mean colour of the separate phosphorescences of the active substances present, and (5) in the preparation of the sulphide the best temperature is a cherry-red heat, but if this temperature be exceeded or the action of heat be too prolonged, the product will probably be non-phosphorescent.

C. H. B.

Sulphantimonites of Barium, Strontium, and Calcium. By POUGET (*Compt. rend.*, 1898, 126, 1792—1793).—*Barium orthosulphantimonite*, $\text{Ba}_3\text{Sb}_2\text{S}_6 + 8\text{H}_2\text{O}$, obtained by warming antimony sulphide with a solution of barium sulphide or barium hydrogen sulphide, crystallises in small, white scales, which become yellow on exposure to dry air. When antimony sulphide is treated with barium sulphide solution in the cold, *barium pyrosulphantimonite*, $\text{Ba}_3\text{Sb}_2\text{S}_5 + 8\text{H}_2\text{O}$, is obtained as a greenish-grey, crystalline mass. Both these salts are

decomposed by water with formation of a chestnut-yellow, amorphous compound of the composition $\text{Ba}_3\text{Sb}_4\text{S}_9 + 10\text{H}_2\text{O}$.

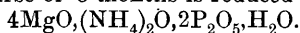
Strontium orthosulphantimonite, $\text{Sr}_3\text{Sb}_2\text{S}_6 + 10\text{H}_2\text{O}$, obtained in a similar manner to the barium salt, crystallises in white scales. By evaporating the mother liquor, small yellow crystals of the *pyrosulphantimonite*, $\text{Sr}_2\text{Sb}_2\text{S}_5 + 15\text{H}_2\text{O}$, are obtained. The same salt is produced by the action of strontium sulphide solution on antimony sulphide in the cold. It is soluble in water without appreciable decomposition.

Calcium pyrosulphantimonite, $\text{Ca}_2\text{Sb}_2\text{S}_5 + 15\text{H}_2\text{O}$, obtained by warming antimony sulphide with calcium hydrogen sulphide solution, and evaporating the liquid in a vacuum, forms large, colourless crystals which, like those of the strontium salt, belong to the anorthic system and are soluble in water without decomposition. If the solution, however, is concentrated by heating, a compound of the formula SbS_2CaOH is formed, which crystallises in red scales and is insoluble in water.

All the compounds described are readily oxidised by exposure to air, and should be prepared in a current of hydrogen. It may be observed that the analogy between calcium and strontium is shown in the pyro-salts, and that between strontium and barium in the ortho-salts.

N. L.

Magnesium Phosphates. By HEINRICH STRUVE (*Zeit. anal. Chem.*, 1898, 37, 485—496).—Magnesium ammonium orthophosphate, as obtained by precipitation, has the formula $\text{MgNH}_4\text{PO}_4 + 6\text{H}_2\text{O}$. The same compound is obtained when the basic magnesium phosphate, $2\text{MgO}, \text{P}_2\text{O}_5, 7\text{H}_2\text{O}$, discovered by the author (*Abstr.*, 1897, ii, 372) is digested with excess of ammonia solution at ordinary temperatures for some months. It is permanent in the air at 30° , but in a desiccator over sulphuric acid (between 25° and 30°) it loses both ammonia and water, and in the course of 3 months is reduced to



Boiled with water, it gives up one-third of its ammonia and half its water, yielding the insoluble compound $6\text{MgO}, 2(\text{NH}_4)_2\text{O}, 3\text{P}_2\text{O}_5, 18\text{H}_2\text{O}$. At higher temperatures, in a current of hydrogen, it loses the whole of its ammonia and water, giving a white residue, which at a red heat becomes incandescent without change of weight, and turns grey from the deposition of traces of carbon derived seemingly from organic substances in the ammonia used for its preparation. This carbon burns off when the residue is heated in oxygen. If the original compound is heated in air instead of in hydrogen, it begins to lose ammonia at 60° , and water at 80° . After the loss of two-thirds of its ammonia and at a low red heat, red vapours, consisting of nitrogen oxides, are given off. The cause of the incandescence is as yet obscure; it sometimes fails to occur with pure preparations, and it is not prevented by an admixture of calcium phosphate. Magnesium ammonium phosphate immersed in glycerol is, at ordinary temperatures slowly, at high temperatures rapidly, converted into $2\text{MgO}, \text{P}_2\text{O}_5 + 7\text{H}_2\text{O}$.

M. J. S.

Beryllium Iodide. By PAUL LEBEAU (*Compt. rend.*, 1898, 126, 1272—1275).—When beryllium carbide is heated at about 700° in a

current of hydrogen, or, better, dry hydrogen iodide, carrying iodine vapour, it is readily converted into beryllium iodide, which condenses in colourless crystals, of sp. gr. = 4.2 at 15°. Traces of ferric iodide can be removed, if necessary, by resublimation in a current of carbonic anhydride.

Beryllium iodide alters readily in moist air; it melts at about 510°, and partially sublimes before melting, but boils between 585° and 595°. It distils without change in an atmosphere of hydrogen or nitrogen, but when heated in air it burns below a red heat. It is readily decomposed by fluorine, chlorine, bromine, cyanogen, hydrogen sulphide, sulphur, sodium, potassium, lithium, and magnesium, but not by aluminium, copper, or mercury below the softening point of glass. It reacts with a large number of carbon compounds, especially those containing oxygen, but has no action on carbon tetrachloride or dichloride. With ammonia, it forms the compound $2\text{BeI}_2 \cdot 3\text{NH}_3$, and it also yields crystallisable products with aniline, pyridine, and other organic bases. When crystallised, the iodide very readily combines with water, but it is more stable after being melted. It is insoluble in most organic solvents, except alcohols, with which it forms crystalline compounds.

C. H. B.

Preparation and Properties of Anhydrous Beryllium Fluoride and Oxyfluoride. By PAUL LEBEAU (*Compt. rend.*, 1898, 126, 1418—1421).—The product described by Berzelius as anhydrous beryllium fluoride, obtained by dissolving the oxide in hydrofluoric acid, evaporating to dryness, and drying at 100°, always contains water, and on heating to redness yields an oxyfluoride, which analysis shows to have the composition $5\text{BeF}_2 \cdot 2\text{BeO}$. This is a colourless, nearly transparent, solid, readily soluble in water, and having a sp. gr. = 2.01 at 15°. Anhydrous beryllium fluoride may, however, be obtained by heating the moist substance to redness in a current of hydrogen fluoride, or by igniting the double fluoride of ammonium and beryllium in an atmosphere of carbonic anhydride. It is a deliquescent, vitreous solid of sp. gr. = 2.1 at 15°, which softens on heating, becomes quite fluid at about 800°, and finally volatilises with formation of a crystalline sublimate. It dissolves in water in all proportions, and is also soluble in alcohol. Oxygen converts it into the oxyfluoride, but the vapour of sulphur is without action. It is decomposed by sulphuric acid, and also on heating to redness with potassium, sodium, or magnesium. Beryllium fluoride is insoluble in anhydrous hydrofluoric acid, a fact which renders improbable the existence of beryllium hydrogen fluoride.

N. L.

Beryllium Borocarbide. By PAUL LEBEAU (*Compt. rend.*, 1898, 126, 1347—1349).—When a mixture of beryllium oxide (75 parts) and boron (45 parts), contained in a carbon crucible, is heated for a short time in the electric furnace, a compound is formed which analysis shows to have the composition $\text{C}_4\text{B}_6\text{Be}_6$. *Beryllium borocarbide* forms brilliant crystals of metallic lustre, having a sp. gr. = 2.4, and readily soluble in mineral acids. It is not altered by exposure to air at the ordinary temperature, but suffers superficial oxidation on

heating to redness; it burns in chlorine at about 450° with production of boron chloride, beryllium chloride, and amorphous carbon.

N. L.

Atomic Weight of Cadmium. By HARMON N. MORSE and H. B. ARBUCKLE (*Amer. Chem. J.*, 1898, 20, 536—542).—The authors have repeated the experiments of Morse and Jones (*Abstr.*, 1892, 1397) on the atomic weight of cadmium, taking into account the weight of gas occluded by the oxide formed on igniting cadmium nitrate. The occluded gas, consisting entirely of oxygen and nitrogen, was analysed by the method previously adopted by the authors in determining the atomic weight of zinc (this vol., ii, 334). No trace of nitric oxide could be detected in the cadmium oxide obtained in the several determinations. On account of the volatility of cadmium oxide at high temperatures, the crucibles containing the nitrate were maintained at a temperature intermediate between the fusing points of sodium chloride (776°) and potassium carbonate (835°); under these conditions, no volatilisation occurred. The amount of mixed gases occluded per gram of cadmium oxide varied in nine experiments from 0.243 to 0.262 c.c.; none of this was removed by exposure under water in a vacuum, or on boiling with water under atmospheric pressure.

The average of nine experiments, ranging from 112.359—112.395 gives 112.377 as the corrected value for the atomic weight of cadmium (oxygen = 16). This agrees very closely with the values 112.39 and 112.38 obtained by Bucher, working with the chloride and bromide of the metal.

W. A. D.

Metallic Precipitation. By DONATO TOMMASI (*Bull. Soc. Chim.*, 1897, [iii], 17, 440—441).—In his work on metallic precipitation (*Abstr.*, 1897, ii, 171), Senderens omits all mention and appears to be ignorant of the fact that the author had already fully investigated the action of aluminium on solutions of copper chloride in 1882.

H. C.

Alloys. By M. HERSCHKOWITSCH (*Zeit. physikal. Chem.*, 1898, 27, 123—166).—Notwithstanding the work of Laurie (*Trans.*, 1894, 1030) on the E. M. F. of alloys, of Matthiesen on their electrical conductivity (*Phil. Trans.*, 1860, 150, 161), and of others, the existence of actual chemical compounds in alloys is still doubtful, and the author therefore investigated the question in a manner similar to that adopted by Laurie, that is, by the determination of the difference of potential between the alloy and the pure metal in a voltaic cell, employing as electrolyte a solution of a salt of the metal under examination, a necessity not observed by Laurie. The following cases are possible. (1) The metals are present in the pure state, or the alloy is a mechanical mixture; the potential in this case is constant, being that of the less noble metal. (2) The metals are partially soluble; the potential is constant during the existence of the same two phases, but when one phase, that is, the metal previously in excess, disappears, the potential takes a value intermediate between the previous value and the final. (3) The metals are completely soluble; the potential varies

continuously between the extreme values. (4) Chemical compounds are formed; in this case, a sudden change of potential occurs at a concentration which is that of the compound. Alloys of the following pairs were examined, the composition in each case being varied within very wide limits. Cadmium-lead, cadmium-tin, cadmium-bismuth, zinc-tin, zinc-bismuth, copper-silver, zinc-copper, zinc-silver, zinc-antimony, tin-copper, and tin-silver; the potential was in all cases measured against that of the first named metal in a solution of one of its salts. In the case of the first six pairs, the potential of the alloy remained constant until a very low percentage of the first metal was reached, when it continuously fell to the second value, that is, the alloys were of the second kind. In all the other pairs of alloys, a compound was indicated by a sudden fall of potential, the compounds being respectively, Zn_2Cu , Zn_4Ag , ZnSb_2 , Cu_3Sn , Ag_4Sn ; the formation of the two last compounds is in accord with previous observations. Alloys of copper-antimony, bismuth-antimony, gold-silver, and aluminium-tin could not be investigated, as the last alloy decomposed water, whilst in the others the potentials of the components are too nearly equal. The heat of formation of some of the alloys was also determined by measuring the heat of formation of the bromides from moist bromine. In all the cases examined, the values differed from those calculated for the mixture, even when the potential determinations indicate no chemical compound. A maximum occurs in the copper-tin at a concentration represented by Cu_3Sn ; in the case of the copper-zinc curve, no such analogous maximum occurs, but the heat development is so slight that its presence might be masked by the experimental errors.

L. M. J.

Equilibrium of a Tertiary System: Lead, Tin, Bismuth. By GEORGES CHARPY (*Compt. rend.*, 1898, **126**, 1569—1573).—Lead, tin, and bismuth mix in all proportions, and form neither definite compounds, nor solid solutions, nor isomorphous mixtures. An alloy of the three metals, therefore, presents the simplest possible case of a system of three constituents in which there are three solid phases, but one liquid phase. The author has determined the melting points of a large number of such alloys, and represents the results by means of one of Thurston's triangular diagrams. Each alloy is represented by a point within an equilateral triangle, at distances from the sides proportional to the relative quantities of the three metals. The angles represent the pure metals, and points on the sides represent binary alloys. The melting points of the alloys are represented by perpendiculars, the heights of which are proportional to the melting points, and the locus of the upper extremities of these perpendiculars is a surface which represents the relation between the melting points of the alloys and their composition. The author first determined the melting points of a number of alloys represented by points falling on one straight line, for example, constant proportions of lead and bismuth, with variable proportions of tin, or constant proportions of lead and tin with variable proportions of bismuth. From the plane curves thus obtained, the isothermals of the surface can be constructed by graphic interpolation. The eutectic mixture of the three metals contains 32

per cent. of lead, 16 per cent. of tin, and 52 per cent. of bismuth, and melts at 96° . An examination of the surface makes it possible to predict the behaviour of any other alloy as it cools from a temperature above its melting point.

C. H. B.

Constitution of Ternary Alloys. By GEORGES CHARPY (*Compt. rend.*, 1898, 126, 1645—1648. Compare *Abstr.*, 1897, ii, 406).—The solidification of an alloy of lead, tin, and bismuth takes place in three stages characterised by definite temperatures. In the first stage, a pure metal separates, either lead, tin, or bismuth, according to the percentage composition of the alloy; in the second, a mixture of two of these metals separates, and in the third stage, all three metals are deposited simultaneously. The existence of the three different deposits is readily proved by microscopic examination of a thin polished section of the alloy, etched with dilute hydrochloric acid. An alloy containing 74.5 per cent. of bismuth, 5.5 per cent. of lead, and 20 per cent. of tin was by this means seen to consist of (1) large tablets of bismuth, deposited at 175° ; (2) a mixture of these with fragments of tin, deposited at 125° ; (3) a eutectic mixture of all three metals, deposited at 96° , which, under a low power, appears to be homogeneous, but is seen, when more highly magnified, to consist of distinct grains of its individual constituents. Alloys of copper, tin, and antimony contain the well-defined compounds SnCu_3 and SbCu_2 (*loc. cit.*), but what has been said with regard to mixtures of lead, tin, and bismuth, also applies to these alloys, assuming the latter to consist, not of copper, tin, and antimony, but of copper, SnCu_3 , and SbCu_2 .

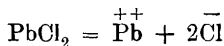
Copper-tin-antimony, lead-copper-antimony, lead-tin-antimony, and zinc-tin-antimony alloys were also examined, and in no case was the formation of a ternary compound observed, only such compounds as are contained in binary alloys being found. In alloys of copper, tin, and antimony, for example, crystals of the compounds SbSn and SnCu_3 were noticed.

In ternary alloys, three successive deposits may, in general, be distinguished. The first is formed by a pure substance which may be either a metal or a compound; the second is a mixture of two substances, one of which is that first deposited; the third is a mixture of three substances which include the two previously deposited. The number of deposits may in certain cases be reduced to two, or even to one, in consequence of the formation of solid solutions. The nature of the successive deposits and their relative proportion depend on the chemical composition of the alloy; the size and distribution of the constituents, and, consequently, the physical and mechanical properties of the alloy, vary, however, with the rapidity of its solidification and other circumstances.

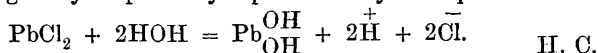
N. L.

Constitution of Lead Salts in Aqueous Solutions. By H. FR. FERNAU (*Zeit. anorg. Chem.*, 1898, 17, 327—354).—The interest which attaches to the behaviour of lead salts in aqueous solutions, in view of the use of these salts in accumulators, has led the author to submit solutions of lead chloride to cryoscopic and electrical investigation. The measurements carried out show that the molecule of lead chloride

undergoes electrolytic dissociation in accordance with the equation



and also that in all probability hydrolysis occurs in very dilute solution. This last change may be probably represented by the equation



Some Halogen Salts of Lead. By VICTOR THOMAS (*Compt. rend.*, 1898, 126, 1349—1352).—Lead chloridide, PbCl_2 , appears to be the sole product of the action of hydrochloric acid and alkali chlorides on lead iodide, and of alkali iodides on lead chloride. This salt is less soluble than either lead chloride or lead iodide, and may be separated therefrom by fractional crystallisation. It is converted by the action of nitric peroxide, even at the ordinary temperature, into lead oxychloride, Pb_2OCl_2 , with elimination of iodine; lead iodide, under the same conditions, yields lead oxide, whilst the chloride and bromide are not affected. N. L.

Mixed Haloids and Halo-thiocyanates of Lead. By CHARLES H. HERTY and T. R. BOGGS (*J. Amer. Chem. Soc.*, 1897, 19, 820—824. Compare Abstr., 1896, ii, 474).—An examination has been made of the crystals deposited from solutions containing two of the lead haloids or one of these salts, and lead thiocyanate, with the object of determining whether mixed crystals or a true compound were formed. Solutions were prepared containing the salts in different proportions, and were submitted to fractional crystallisation, each crop of crystals being examined.

Lead thiocyanate forms a compound with lead chloride and with lead bromide, but not with the iodide, the latter crystallising side by side with the thiocyanate from a mixed solution.

Lead chloride forms mixed crystals with all proportions of the isomorphous bromide, whilst the mixed crystals of chloride and iodide always contain an excess of the former. Similarly, the mixed crystals of bromide and iodide contain an excess of bromide. A. H.

Copper Alkali Thiosulphates. By ARTHUR ROSENHEIM and S. STEINHÄUSER (*Ber.*, 1898, 31, 1876—1877. Compare Ch. and J. Bhaduri, this vol., ii, 428, and Muthmann and Stützel, this vol., ii, 513).—A preliminary notice. The following compounds have been prepared:— $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{K}_2\text{S}_2\text{O}_3 + 1\frac{1}{2}\text{H}_2\text{O}$, yellow, crystalline; $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{K}_2\text{S}_2\text{O}_3 + 1\frac{1}{2}\text{H}_2\text{O}$, yellow prisms; $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{K}_2\text{S}_2\text{O}_3$, white needles; $\text{Cu}_2\text{S}_2\text{O}_3 \cdot (\text{NH}_4)_2\text{S}_2\text{O}_3 + 1\frac{1}{2}\text{H}_2\text{O}$, yellow prisms; $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2(\text{NH}_4)_2\text{S}_2\text{O}_3 + 1\frac{1}{2}\text{H}_2\text{O}$, white needles; $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{BaS}_2\text{O}_3 + 4\text{H}_2\text{O}$, crystalline, white precipitate. Of these, the first two have been described already, but as containing different amounts of water of crystallisation; the third is regarded by Muthmann and Stützel as $\text{K}_2\text{S}_2\text{O}_3 \cdot \text{CuS}_2\text{O}_3$. C. F. B.

Colloidal Mercury. By ALFRED LOTTERMOSER (*J. pr. Chem.*, 1898, [ii], 57, 484—487).—Stannous oxide, prepared by boiling stannous chloride with sodium carbonate and a little water, and washing the precipitate, is dissolved in nitric acid. Into this solution of stannous nitrate, a solution of mercurous nitrate is poured, the mixture being

stirred during the process; both solutions must be very dilute, and contain only enough free acid to prevent the precipitation of a basic salt; a not inconsiderable excess of stannous nitrate must be employed, otherwise the product is unstable. To the dark brown solution thus obtained, ammonium citrate is added, when the colour changes to black, and the coagulated mercury separates as a black precipitate. The liquid is cautiously neutralised with ammonia, and the precipitate is collected and dried over sulphuric acid under diminished pressure. It has a silvery lustre, and dissolves in water, giving a deep brown solution; when chlorine water is added gradually to this, a milky solution of colloidal mercurous chloride is obtained at first; finally, a clear solution of mercuric chloride. Bromine water acts in the same way. In the action of iodine solution, two stages cannot be recognised; a deep red liquid is obtained, which rapidly deposits mercuric iodide.

C. F. B.

Reactions between Mercury and Concentrated Sulphuric Acid. By CHARLES BASKERVILLE and F. W. MILLER (*J. Amer. Chem. Soc.*, 1897, 19, 873—877).—Sulphuric acid reacting with excess of mercury produces sulphurous anhydride and white, crystalline, mercurous sulphate. When a mixture containing excess of acid is heated at 100° for 20 hours, sulphurous anhydride and mercurous sulphate are obtained, and on heating at 150° for 2 hours, a mixture of mercurous and mercuric sulphates is produced, containing 50 per cent. of the former salt; as the temperature is raised, however, the amount of mercurous sulphate diminishes until, when mercury is added to the boiling acid, the product consists entirely of mercuric sulphate. When mercurous sulphate, or a mixture of this with mercuric sulphate, is heated with sulphuric acid, the amount of sulphurous anhydride evolved is proportional to the quantity of mercurous salt present. No indication could be obtained of the liberation of hydrogen during the initial stages of the reaction, and no sulphide or free sulphur was produced. The acid is directly reduced by the metal, and the authors find that this action takes place even at ordinary temperatures.

G. T. M.

Valency of the Cerite Metals. By WILHELM MUTHMANN (*Ber.*, 1898, 31, 1829—1836).—It is impossible to accept Wyruboff's conclusion (*Bull. soc. franç. Min.*, 15, 63), that cerium, lanthanum, didymium, and thorium must be bivalent because they form silicotungstates isomorphous with the calcium salt $12\text{WO}_3, \text{SiO}_2, 2\text{CaO} + 27\text{H}_2\text{O}$, and for other reasons; for, in the first place, the crystalline form of such complex salts is probably but little dependent on the relatively small amount of metallic oxide present; then Bodmann has shown (this vol., ii, 435) that neodymium nitrate forms mixed crystals with bismuth nitrate, from which the tervalency of the cerite metals may equally be inferred. Again, there is no reason, *à priori*, why the ignited oxide of a tervalent metal, such as lanthanum, should not combine with water, to form a slightly soluble hydroxide having an alkaline reaction; as regards absorption of carbonic anhydride, ignited lanthanum oxide no more does this at the ordinary temperature than calcium oxide does. And touching the solubility of the sulphates, anhydrous cerium sulphate is more soluble in cold water than even magnesium sulphate.

The author has now found that the increase in the equivalent conductivity of lanthanum salts with increasing dilution of their aqueous solutions is in accordance with the tervalency of the metal, this increase, $\mu_{32}-\mu_{1024}$, being 28 and 26 for the nitrate and chloride, as compared with 20 and 18 for the corresponding salts of magnesium, whilst for the sulphate it is 47, the values for chromium and aluminium being 59 and 53 respectively.

Further, the molecular weight of cerium chloride, as determined by the boiling point method, in absolute alcoholic solution, is 232; CeCl_3 requires 246.5; CeCl_2 , 164. It must, then, be admitted that the cerite metals are indeed trivalent.

C. F. B.

Incandescent Gas Mantles of Commerce. By ERNEST HINTZ (*Zeit. anal. Chem.*, 1898, **37**, 504—524).—In continuation of earlier work on this subject (this vol., ii, 339), the author has investigated the influence of the addition to the standard mixture of 1 part of ceria and 99 parts of thoria, of quantities of zirconia, neodymia, lanthana, and yttria up to 20 per cent. Zirconia has no influence below 1 per cent., whilst above 1 per cent. it reduces the emissive power. The other earths have no effect up to 2 per cent., but above that limit all of them produce a diminution in the luminosity. Further experiments with different mixtures of thoria and ceria show that any variation in either direction from 1 per cent. of ceria results in diminished luminous effect. When the proportion of ceria does not exceed 1 per cent., and only small quantities of the other earths are present, the percentage of ceria may be approximately ascertained by photometric measurements.

M. J. S.

Earths of the Yttria Group in Monazite Sand. By O. BOUDOUARD (*Compt. rend.*, 1898, **126**, 1648—1651).—The author describes a series of fractionations of earths of the yttria group obtained from monazite sand, effected by fractional decomposition of the nitrates at 325°. Solutions of the sulphates of the earths showed a feeble absorption spectrum, consisting of bands at $\lambda 657-663$, $\lambda 643-639$, $\lambda 537$, and $\lambda 524-522$. The minimum value obtained for the atomic weight of the element contained in the fractions was 96.7, a number considerably higher than the atomic weight of yttrium. The bearing of the results obtained by the author and other observers on the possible existence of a new earth is briefly discussed.

N. L.

Chemistry of Didymium. By LOUIS M. DENNIS and EMILE M. CHAMOT (*J. Amer. Chem. Soc.*, 1897, **19**, 799—809).—The separation of neodymium from praseodymium by Welsbach's method can be most effectively and rapidly carried out in the presence of lanthanum salts by the slow crystallisation of the fractions. In the absence of lanthanum, crystallisation takes place much more slowly and the separation effected is also much less complete. The saturated solutions of the double ammonium nitrates were therefore allowed to crystallise spontaneously, the mother liquor being poured off and treated in the same way, whilst the crystals were redissolved and again allowed to crystallise out spontaneously, fractions giving a similar spectroscopic appearance being

united, irrespective of their position in the series of fractionations. Lanthanum nitrate is added as the neodymium end of the series is approached.

The authors have obtained fractions in which certain of the bands show greatly increased intensity, and consider that the occurrence of these indicates the compound nature of the two constituents of didymium.

A. H.

Action of Nitric Acid on Aluminium. By THOMAS B. STILLMAN (*J. Amer. Chem. Soc.*, 1897, 19, 711—716).—It is generally stated that nitric acid, whether strong or dilute, is without action on aluminium, but Lunge and Schmidt (*Zeit. angew. Chem.*, 1892, 7) found that the metal is readily attacked at ordinary temperatures by nitric acid of sp. gr. 1.20, and that the action diminishes as the concentration of the acid increases; the author's experiments confirm these observations. Coarse turnings containing 99.6 per cent. of aluminium, and nitric acid of three strengths (sp. gr. = 1.15, 1.35, and 1.46) were employed, and in each case 1 gram of the metal was placed in 100 c.c. of acid. The metal completely dissolved at 100°, the time required varying from 20 minutes to 2 hours; after 7 days immersion in the weakest acid at 20°, about 94 per cent. of the sample had dissolved, whilst in the strongest acid under these conditions, only 12 per cent. had passed into solution.

From the solutions thus obtained, aluminium nitrate having the composition $\text{Al}_2(\text{NO}_3)_6 + 18\text{H}_2\text{O}$ separates in colourless, rhombic octahedral crystals.

G. T. M.

Reduction of Permanganic Acid by Manganese Dioxide. By HARMON N. MORSE and CHARLES L. REESE (*Amer. Chem. J.*, 1898, 20, 521—535).—From the fact that no oxygen is evolved when hydrogen is left in contact with a neutral solution of potassium permanganate (compare Meyer and von Recklinghausen, *Abstr.*, 1897, ii, 19), whereas it is rapidly generated when sulphuric acid is present, Hirtz and Meyer (*Abstr.*, 1897, ii, 93) concluded that its production in the latter case could not be attributed to the reducing action on the permanganate of precipitated manganese dioxide (compare Morse, Hopkins, and Walker, *Abstr.*, 1896, ii, 475; and Morse, *Abstr.*, 1897, ii, 145). In support of this view, they adduced the fact that only 12.5 per cent. of the volume of oxygen obtained when hydrogen is present is liberated, in the same time, from an acidified 5 per cent. solution of potassium permanganate by the manganese dioxide precipitated by the hydrogen.

In the author's opinion, this experiment proves only that the oxygen is evolved much more rapidly during the absorption of the hydrogen than is subsequently the case when the precipitated manganese dioxide interacts with the permanganic acid. They suggest, provisionally, that this is due to the manganese dioxide molecules, initially precipitated by a gaseous reducing agent, being of a greater simplicity, and hence capable of more rapid action, than those produced by a solid such as manganous sulphate. From the experiments which follow, they are also led to discredit Hirtz and Meyer's view (*loc. cit.*), that the libera-

tion of oxygen from potassium permanganate by manganese dioxide and by hydrogen or carbonic oxide are phenomena of different orders.

Three solutions, A, B, and C, were employed, containing respectively 2·822, 5·644, and 51 milligrams of potassium permanganate per c.c.; each solution was carefully freed from precipitated manganese dioxide before use. The first two of these did not lose any measurable quantity of oxygen when agitated, either neutral or strongly acid, in contact with air in sealed tubes, during 150—300 hours. The third solution, C, however, which, while neutral or only slightly acid, was not decomposed at all under these conditions, liberated from 1·9 to 3·6 c.c. of oxygen when acidified with an amount of dilute sulphuric acid equivalent to three times the potassium of the salt. Since this solution was much more stable than Meyer and Recklinghausen's 5 per cent. solution, the authors conclude that the latter contained manganese dioxide, precipitated either by the addition of *concentrated* sulphuric acid, or by the subsequent heating to which it was subjected.

Experiments made to determine the relative rates of reduction when equal volumes of permanganic acid are agitated, on the one hand, with a certain volume of hydrogen, and, on the other, with a quantity of manganese dioxide, precipitated by manganous sulphate, equivalent to the latter, show: (1) That in the case of the solutions B and C, the oxide precipitated by hydrogen is by far the more active one, during the first 24 hours; in the case of solution A, the hydrogen was not completely absorbed in this time. (2) That the maximum rapidity of action of the hydrogen as an oxygen liberator occurs when the concentrated solution C is acidified with 3 mols. of sulphuric acid; 19·88 c.c. of oxygen were evolved in 24 hours, whilst from the precipitated manganese dioxide, in the same time, only 2·5 c.c. were obtained. This confirms Hirtz and Meyer's crucial experiment. (3) That in the period from the 24th to the 150th hour, the oxide produced by hydrogen acts much less rapidly in solution C than that produced by manganous sulphate. In the case of B, and possibly of A, the order of activity is reversed; but with all three solutions between the 150th and 300th or 600th hour, the oxide from the hydrogen is much the less active. (4) That assuming the liberation of oxygen by hydrogen to be due to precipitated manganese dioxide, the evidence appears to show that this action is continuous, and without any such limit as was thought to exist by Meyer and von Recklinghausen. W. A. D.

[NOTE BY ABTRACTOR.—In the original paper, the authors have apparently misinterpreted (p. 522) Hirtz and Meyer's objection to the hypothesis that manganese dioxide is the cause of the liberation of oxygen during the hydrogen absorption. Its point appears to be, that when neutral potassium permanganate is employed, no oxygen is evolved, although here, as well as with acid solutions, manganese dioxide is precipitated.]

Vaporisation of Iron at the Ordinary Temperature. By HENRI PELLAT (*Compt. rend.*, 1898, 126, 1338. Compare Abstr., 1896, ii, 601).—The action of iron on a photographic plate in the dark must be attributed to vaporisation of the iron, and not to radiations

emitted by it, since the phenomenon does not occur when the metal is separated from the plate by a thin sheet of glass. N. L.

Minute Structure of Alloys of Iron and Nickel. By FLORIS OSMOND (*Compt. rend.*, 1898, 126, 1352—1354).—The study of the minute structure of alloys of iron and nickel confirms the classification based upon mechanical properties and the analogy between this series of alloys and the various carbon and manganese steels. Three distinct groups may be recognised: (1) Alloys containing up to about 8 per cent. of nickel; structure resembling that of ordinary steel, except that the grains of iron are smaller and show a less tendency to increase in size at high temperatures. (2) Alloys containing from 12 to 25 per cent. of nickel; structure fibrous, like that of tempered carbon steels. (3) Alloys containing from 25 to 50 per cent. of nickel; structure purely crystalline. N. L.

Influence of Heat Treatment, and of Carbon, on the Solubility of Phosphorus in Steel. By EDWARD D. CAMPBELL and S. C. BABCOCK (*J. Amer. Chem. Soc.*, 1897, 19, 786—790. Compare Abstr., 1897, ii, 101).—Experiments similar to those previously described have been made with an accurate pyrometer, so that the exact temperatures employed are known. The percentage of phosphorus soluble in a slightly acid solution of mercuric chloride was estimated in samples, containing various amounts of carbon, which were submitted to different heat treatment. The results confirm the conclusion that phosphorus, like carbon, is capable of existing in steel in at least two forms, and that the influence of phosphorus on the physical properties of steel is as much dependent on the form of combination as on the quantity present. A. H.

Condition of Silicon and Chromium in Irons and Steels. By ADOLPHE CARNOT and GOUTAL (*Compt. rend.*, 1898, 126, 1240—1245). Ferrosilicons poor in manganese contain a silicide, SiFe_3 , which is magnetic, and can be isolated by dissolving the metal in very dilute sulphuric acid and treating the residue successively with potassium hydroxide solution and dilute sulphuric acid. It is identical in composition with the silicide obtained by Moissan in the electric furnace, but differs from it in being readily attacked by hot dilute acids.

Silico-spiegels containing 20 per cent. of manganese contain a double silicide, $\text{Si}(\text{Fe}:\text{Mn})_3$. Ferromanganeses contain the silicide SiFe_2 , which also exists in the ferrosilicons poor in manganese.

Ferrochromiums, when treated with hydrochloric acid at 60° , the residue being afterwards fused with potassium hydrogen sulphate, yield an insoluble residue of the iron chromium carbide, $\text{CFe}_3\cdot 3\text{C}_2\text{Cr}_3$.

Chrome steels contain the carbide, $3\text{CFe}_3\cdot \text{Cr}_2\text{C}_3$, which can be isolated by treatment with very dilute (7:100) hydrochloric acid, and the same carbide was also isolated from a ferromanganese containing a small quantity of chromium by treating it with cupric potassium chloride solution (compare Abstr., 1897, ii, 555). C. H. B.

Hydrolysis of Ferric Chloride. By WALTHER SPRING (*Rec. Trav. Chim.*, 1897, 16, 237—249. Compare Krecke, *J. prakt. Chem.*, 1871, [ii], 3, 286; Wiedemann, *ibid.*, 1874, [ii], 9, 145; Antony and Giglio, Abstr., 1896, ii, 250, and Goodwin, Abstr., 1897, ii, 16).—In opposi-

tion to former views, it is stated that ferric chloride, when in solution, undergoes exactly the same dissociation as when heated. It is first converted into ferrous chloride and chlorine, the latter then reacts with the water, yielding hydrogen chloride and oxygen, the oxygen combines with the ferrous chloride, yielding an oxychloride, $\text{Fe}_2\text{Cl}_4\text{O}$, which, with the water and hydrochloric acid, forms a state of equilibrium varying with the temperature.

Most of the author's experiments were restricted to concentrated solutions. When solid potassium ferricyanide and resublimed ferric chloride are ground together, no reaction takes place; the same is true if a very concentrated solution (230 in 100) of ferric chloride is used. More dilute solutions (below 126 in 100) give an immediate precipitate of Prussian blue and chlorine is evolved; with still more dilute solutions (5 or 10 in 100) a brown coloration is developed, and finally a blue precipitate is formed. It is not possible to fix a limit of dilution at which the blue precipitate is not immediately formed; in fact, a mixture which at ordinary atmospheric pressure gives no immediate precipitate, gives the blue precipitate on the surface when placed under reduced pressure. It has also been found that solutions of ferric chloride of different strengths, after being charged with chlorine, yield no precipitate with potassium ferricyanide, unless they are placed under reduced pressure.

Ferric bromide reacts in much the same manner, but since it is more readily dissociated, more concentrated solutions react with potassium ferricyanide, yielding the blue precipitate and evolving bromine. Ferric nitrate, on the other hand, reacts much more slowly.

Reference is also made to ferric and ferrous iodides.

If air is drawn through concentrated solutions of ferric chloride, hydrogen chloride, and not chlorine, is evolved; dilute solutions yield neither. Saturated solutions of ferric chloride have very little action on metallic iron, less concentrated solutions readily dissolve the metal, and it has been found that the metal is most readily dissolved by those solutions which give an immediate blue precipitate when treated with potassium ferricyanide. In solutions the concentration of which is less than 80 in 100, evolution of hydrogen always accompanies dissolution of the metal. The facts are in accord with the theory of hydrolysis stated above.

The hydrolysis is to be compared to ionisation, the ferrous chloride becoming cathion and the chlorine anion. A difference of potential can be shown to exist between the two.

J. J. S.

Ferric Phosphate. By ROBERT M. CAVEN (*J. Soc. Chem. Ind.*, 1896, 15, 17—19 and 70).—On gradually adding a neutral solution of ferric chloride to a solution of ammonium phosphate, a precipitate is at first formed, which subsequently redissolves, giving a clear solution when the quantity of ferric chloride necessary to form ferric phosphate has been added. In presence of ammonium acetate and a few drops of acetic acid, however, a precipitate of ferric phosphate is obtained. The latter is best prepared by adding ferric chloride to twice the theoretical amount of phosphoric acid dissolved in water; on washing the precipitate with hot water, slight hydrolysis appears to

take place, with the formation of phosphoric acid and ferric hydroxide. Fresenius has stated that the estimation of phosphoric acid as ferric phosphate is inaccurate, owing to the latter being slightly soluble in water; in the author's opinion, the salt is insoluble in water, but loses phosphoric acid when washed in the manner above stated. By long-continued boiling with an excess of aqueous ammonia, ferric phosphate is completely converted into ferric hydroxide and ammonium phosphate; the reverse change, however, takes place when freshly precipitated ferric hydroxide is boiled with aqueous ammonium phosphate, ammonia being evolved and ferric phosphate formed.

On digesting an excess of ferric phosphate with cold, dilute hydrochloric acid, and filtering, a solution is obtained which is almost colourless. It appears to contain free hydrochloric acid and dissolved ferric phosphate; double decomposition, however, seems to occur on adding concentrated hydrochloric acid, as a yellow coloration is immediately produced.

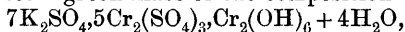
W. A. D.

Preparation of Cobalt-ammonia Salts. By SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1898, 17, 455—479).—The paper contains details of the methods of preparation and of identification employed by the author. It is chiefly a *résumé* of the work previously published by the author and others.

E. C. R.

Colour Changes in Solutions of Chromium Salts. By FRANCIS P. VENABLE and F. W. MILLER (*J. Amer. Chem. Soc.*, 1898, 20, 484—497).—It is well known that solutions of certain chromium salts which are violet in colour become green on heating. A reverse action takes place on standing, the solutions regaining their green colour; some salts, however, require a much longer time than others for this change to become complete. The authors consider that the most likely explanation of these changes is that brought forward by Berzelius (*Ann. phys. Chem.*, 61, 1), and which presupposes the formation of basic chromium salts (compare Dougal, *Trans.*, 1896, 1526).

When alcohol is added to the violet solution of chrome alum, fine violet crystals of the composition $K_2SO_4 \cdot Cr_2(SO_4)_3 + 12H_2O$ are obtained; but from a solution of the alum rendered green by heating, alcohol precipitates a green mass of the composition



and from the green solution of chromium sulphate, salts, probably of the formulæ $Cr_2(SO_4)_3 \cdot Cr_2(OH)_6 + 15H_2O$ and $2Cr_2(SO_4)_3 \cdot Cr_2(OH)_6 + 20H_2O$, are thrown down.

A. W. C.

Action of some Carbonates on Chromous Acetate. By GEORGES BAUGÉ (*Compt. rend.*, 1898, 126, 1566—1569).—When chromous acetate is treated with a 20 per cent. solution of potassium carbonate, the compound $(K_2CO_3 \cdot CrCO_3)_2 + 3H_2O$ is obtained in small, yellow, hexagonal prisms, which at first dissolve in water, but gradually polymerise, whether in solution or in the solid state, and become less soluble. It is a powerful reducing agent, and decomposes water below 100° ; when heated out of contact with air, it becomes brown, but regains its original colour on cooling; at about 280° , it decomposes. When heated in air, it is converted into potassium chromate.

If the yellow double carbonate is placed in water and treated with a current of carbonic anhydride, or if the chromous acetate is treated with a dilute solution of potassium carbonate, a less soluble, red double carbonate is formed, but was not analysed; it is partially decomposed by water, and decomposes water at 100° .

Magnesium hydrogen carbonate converts the chromous acetate into a red-brown compound, which decomposes water at 100° ; but could not be obtained free from magnesium carbonate precipitated at the same time. The carbonates of barium, calcium, and strontium have no action on chromous acetate.

C. H. B.

Blue Glass containing Chromic Oxide as a Basic Constituent. By ANDRÉ DUBOIN (*Ber.*, 1898, 31, 1977—1979).—The blue colour of the sapphire is due to chromium, and can be reproduced by fusing the necessary mixture in a reducing flame. Blue glass containing chromium can readily be prepared by fusing many mixtures of silica, alumina, lime, &c., with potassium chromate in a crucible lined with carbon. The best results are obtained with mixtures containing baryta or boric acid. Calcium carbide can be used as a reducing agent, whereas aluminium does not yield good results. Ordinary glass only gives a product which is violet-blue in the immediate neighbourhood of the layer of carbon.

A. H.

The Lowest State of Oxidation of Molybdenum. By WILHELM MUTHMANN and WILHELM NAGEL (*Ber.*, 1898, 21, 2009—2014).—The authors confirm Blomstrand's view as to the complex nature of the so-called dichloride and dibromide of molybdenum. The formation of the hydroxides, $\text{Mo}_3\text{Cl}_4(\text{OH})_2$ and $\text{Mo}_3\text{Br}_4(\text{OH})_2$, the existence of salts such as $\text{Mo}_3\text{Cl}_4\text{Br}_2$ and $\text{Mo}_3\text{Cl}_4\text{CrO}_4$, and the great stability of the radicles, Mo_3Cl_4 and Mo_3Br_4 , towards alkalis and silver nitrate led Blomstrand to conclude that the above haloids had the formulæ $\text{Mo}_3\text{Cl}_4\text{Cl}_2$ and $\text{Mo}_3\text{Br}_4\text{Br}_2$, and he called them chloromolybdenum chloride and bromomolybdenum bromide respectively.

A determination of the molecular weight of the chloride in alcoholic solution indicates that its formula is Mo_3Cl_6 . An alcoholic solution of the chloride, when electrolysed, yields hydrogen and the hydroxide, $\text{Mo}_3\text{Cl}_4(\text{OH})_2$, at the cathode, whilst aldehyde and ethylic chloride are formed at the anode. When a solution of the salt, $\text{Mo}_3\text{Br}_4(\text{ONa})_2$, is electrolysed, the free hydroxide, $\text{Mo}_3\text{Br}_4(\text{OH})_2$, is produced at the anode, and hydrogen is liberated at the cathode.

On warming the alkaline solution of the chloride or the bromide, a black precipitate is produced, which Blomstrand at first supposed to be the hydrated monoxide, and to which he afterwards gave the formula $\text{Mo}_3(\text{OH})_6$. The authors find that hydrogen is evolved in this reaction and that the precipitate really consists of the hydrated sesquioxide, $\text{Mo}(\text{OH})_3$. From this, it follows that there is no longer any evidence for the existence of the monoxide or of compounds containing bivalent molybdenum.

G. T. M.

Ozomolybdates [Permolybdates]. By WILHELM MUTHMANN and WILHELM NAGEL (*Ber.*, 1898, 31, 1836—1844. Compare this vol., ii, 432).—In the molybdates of the alkali metals it is possible, by digestion with hydrogen peroxide solution, to add on oxygen to the extent

of one atom of oxygen, or *less*, per atom of molybdenum, but the compounds formed are not to be regarded as the salts of permolybdic acid, properly so called; they lose oxygen readily, reducing potassium permanganate and silver oxide, with evolution of oxygen, and it must be supposed that the apparent addition of an atom of oxygen consists really in the replacement of one atom of oxygen by two linked to one another as in hydrogen peroxide or ozone, for which reason the compounds are named *ozomolybdates*.

Ozomolybdic acid, $\text{H}_2\text{MoO}_5 + x\text{H}_2\text{O}$ [$x = 1\frac{1}{2}$?], was obtained by digesting molybdic anhydride with 25 per cent. hydrogen peroxide solution, finally on the water bath, filtering, and concentrating the filtrate under diminished pressure. It is orange-red and amorphous; besides reducing permanganate, silver oxide, and hypochlorites, it liberates the halogens from their compounds with hydrogen. The ozomolybdates were obtained by dissolving molybdates in hydrogen peroxide solution, usually of 25 per cent. strength, with the aid of heat; frequently one compound separated first, and then another; these are described in the order in which they separated. Evidence was obtained of the existence of other ozomolybdates, in addition to those described, but it was impossible to isolate them.

Rubidium ozomolybdates.—From $\text{Rb}_2\text{O}, 3\text{MoO}_3$: (1) $3\text{Rb}_2\text{O}, 10\text{MoO}_4 + 14\text{H}_2\text{O}$, yellowish-red and amorphous; (2) $\text{Rb}_2\text{O}, 2\text{MoO}_3, \text{MoO}_4 + 3\text{H}_2\text{O}$, yellow, monoclinic crystals. From $3\text{Rb}_2\text{O}, 7\text{MoO}_3 + 4\text{H}_2\text{O}$ and 5 per cent. hydrogen peroxide: (1) $\text{Rb}_2\text{O}, 2\text{MoO}_3, \text{MoO}_4 + 3\text{H}_2\text{O}$ (see above); (2) $3\text{Rb}_2\text{O}, 5\text{MoO}_3, 2\text{MoO}_4 + 6\text{H}_2\text{O}$, monoclinic crystals; in one case, when a very dilute solution was prepared, yellow, monoclinic tables of $\text{Rb}_2\text{O}, 3\text{MoO}_3, \text{MoO}_4 + 4\text{H}_2\text{O}$ separated.

Rubidium trimolybdate, $\text{Rb}_2\text{O}, 3\text{MoO}_3$, obtained by fusing Rb_2CO_3 with 3MoO_3 , was once obtained crystallised with $1\text{H}_2\text{O}$.

Cæsium ozomolybdates.—From $\text{Cs}_2\text{O}, 4\text{MoO}_3$: (1) $\text{Cs}_2\text{O}, 4\text{MoO}_4 + 6\text{H}_2\text{O}$, orange-red, amorphous; (2) $3\text{Cs}_2\text{O}, 7\text{MoO}_3, 3\text{MoO}_4 + 4\text{H}_2\text{O}$, yellow, crystalline.

Cæsium tetramolybdate, $\text{Cs}_2\text{O}, 4\text{MoO}_3$, and not a trimolybdate, is obtained by fusing CsCO_3 with 3MoO_3 , and washing the fused mass with water; it crystallises from water with $2\text{H}_2\text{O}$.

The compound, $\text{K}_2\text{O}_2, \text{MoO}_4, \text{H}_2\text{O}_2$, described by Melikoff and Pissarjewsky (this vol., ii, 337), was probably not a definite chemical compound. It may be regarded as certain, however, that at low temperatures molybdates can take up *more* than one atom of oxygen for each atom of molybdenum contained in them.

C. F. B.

A New Carbide of Tungsten. By P. WILLIAMS (*Compt. rend.*, 1898, 126, 1722—1724).—When a mixture of tungstic anhydride and carbon is heated in the electric furnace, the carbide, W_2C , described by Moissan is produced. In presence of a large excess of iron, however, combination occurs at a somewhat lower temperature, and a compound having the composition WC is obtained. This carbide is an iron-grey powder, consisting of microscopic, cubical crystals, which are harder than quartz and have a sp. gr. = 15.7 at 18°. When strongly heated in a closed vessel, it melts and decomposes into graphite and the carbide W_2C , whilst in presence of air or oxygen it slowly

oxidises, with formation of tungstic and carbonic anhydrides. It is attacked by fluorine in the cold with incandescence, but is not acted on by chlorine, bromine, iodine, and the halogen acids. Sulphuric and nitric acids have but little action on the carbide, but it is readily oxidised by heating with potassium chlorate or nitrate. N. L.

Solubility of Stannous Iodide in Water and in Solutions of Hydriodic Acid. By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1897, 19, 845—851).—The solubility of stannous iodide in water increases as the temperature rises. In hydriodic acid solutions containing 3 to 8 per cent. of acid, the solubility is less than in water, increasing with the temperature and diminishing with the concentration of the acid. With solutions of 9 to 15 per cent., the solubility is still less than in water, and increases with the temperature, but it now also increases with the concentration. When the solutions contain 25 per cent. and upwards, the solubility is greater than in water, and as the temperature rises the solubility at first diminishes until a point of minimum solubility is reached lying between 30° and 40°; beyond this, the solubility again increases. G. T. M.

Iodostannous Acid. By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1897, 19, 851—859. Compare previous abstract).—A saturated solution of stannous iodide in hydriodic acid of 25 per cent. and upwards when cooled by ice cold water, deposits pale yellow needles quite different in appearance from the red needles of stannous iodide. This yellow substance readily decomposes, giving the red iodide, and is so unstable that its composition could only be obtained by indirect methods. By determining the amounts of hydrogen and stannous iodides in solution before and after the separation of the yellow solid, this is shown to be an *iodostannous acid* having the formula HSnI_3 .

Hydriodic acid of known strength was taken, and an amount of stannous iodide more than sufficient to saturate the liquid added to it, and finally the amount of stannous iodide dissolved was estimated by titration.

From 0° to 15° the solubility in hydriodic acid of 39.6 per cent. strength increases; and from 15 to 20° it still increases, but much more slowly; on allowing the mixture to remain for some hours at 20°, the undissolved yellow iodostannous acid changes to red stannous iodide, and this change is accompanied by a marked decrease in solubility; from 20° to 30°, the solubility diminishes gradually, and from 30° upwards it increases regularly. With a similar solution in 30 per cent. acid, the rapid decomposition of iodostannous acid occurs at 1.5°, and in this case the change is accompanied by an increase in solubility. When in contact with stronger hydriodic acid, the iodostannous acid is stable at higher temperatures. The peculiarities observed in the curves of solubility are due to the gradual decomposition of solid and dissolved iodostannous acid over a considerable range of temperature.

G. T. M.

Atomic Weight of Zirconium. By FRANCIS P. VENABLE (*J. Amer. Chem. Soc.*, 1898, 20, 119—128).—To prepare the material used in his determinations, the author fused pulverised zircon in a

nickel crucible with a mixture of sodium hydroxide and fluoride; after dissolving in hydrochloric acid, and attempting to remove the silica by evaporating to dryness, it was found that the latter was retained by the zirconium chloride, even after several crystallisations from boiling concentrated hydrochloric acid. The chloride was therefore ignited, and the powdered zirconia strongly heated several times with hydrofluoric acid; the product was fused with potash, dissolved in hydrochloric acid, and the chloride formed crystallised twenty or thirty times from boiling hydrochloric acid. The crystals thus obtained were introduced, in quantities of 1 to 5 grams, into small glass flasks of known weight, and dried at 100° in a stream of hydrogen chloride; on attaining a constant weight, the product consisted of a white powder having the composition $\text{ZrOCl}_2 + 3\text{H}_2\text{O}$. It was dissolved in a small quantity of water, transferred to a platinum crucible, the solution evaporated, and the residue gradually heated during 3 or 4 days until the whole of the chlorine was evolved. The values of the atomic weight of zirconium, obtained by comparing the weight of zirconia thus produced with the weight of the oxychloride taken, range from 90.61 to 91.12; the mean of 10 experiments is 90.78 ($\text{O} = 16$), which compares well with the value 90.65 given by Bailey.

The main sources of error in the method are the deliquescence of the oxychloride; the loss of finely-divided zirconia during ignition; the corrosion of the platinum crucibles; the action of the gaseous and liquid hydrochloric acid on the glass vessels; and substances carried into the drying flasks by the stream of hydrogen chloride. The author purposes repeating the work under conditions which will minimise these errors.

W. A. D.

Zirconium Oxyhaloids. By FRANCIS P. VENABLE and CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1898, 20, 321—329).—*Zirconium oxychloride*, $\text{ZrOCl}_2 + 8\text{H}_2\text{O}$, is obtained when a solution of zirconium hydroxide in hydrochloric acid is evaporated; large crystals are obtained when the solution is evaporated over sulphuric acid; these crystals lose water when exposed to the atmosphere. When heated to 135 — 140° , a large amount of chlorine is driven off, but yet not the whole of the water. When heated at 100° in a current of hydrogen chloride, the crystals lose $5\text{H}_2\text{O}$ (compare Paijkull, this Journ., 1873, 1105, and Melliss, *Zeit. Chem.*, 1870, [ii], 6, 196). A second form of the oxychloride may be obtained by crystallising from concentrated hydrochloric acid and then drying the crystals at 100 — 125° in an atmosphere of hydrogen chloride (compare Linnemann, *Abstr.*, 1885, 1042, and Bailey, *Chem. News*, 1891, 60, 17); the composition of the dried crystals is represented by the formula $\text{ZrOCl}_2 + 3\text{H}_2\text{O}$. A third oxychloride, insoluble in hydrochloric acid, but readily soluble in water, is obtained by precipitating an aqueous solution with hydrochloric acid. Its composition is $\text{ZrOCl}_2 + 6\text{H}_2\text{O}$, although Paijkull represented it as $2\text{ZrOCl}_2 + 13\text{H}_2\text{O}$.

An oxybromide, $\text{ZrOBr}_2 + 8\text{H}_2\text{O}$, has been previously described by Weibull (*Abstr.*, 1887, 778). The authors find that the oxybromides belong to two types with varying degrees of hydration, namely,

$\text{ZrOBr}_2 + x\text{H}_2\text{O}$, where $x = 3, 13$, or 14 , and $\text{ZrBr}(\text{OH})_3 + y\text{H}_2\text{O}$, where $y = 1$ or 2 . All these compounds are deliquescent, and decompose on exposure to moist air, the clear, white crystals often coloured pink by the presence of free bromine, melting to a gum, frequently with the evolution of hydrogen bromide. The salts are unstable even in dry air, as was shown by exposing the crystals in a desiccator over sulphuric acid, when much hydrogen bromide was evolved. The crystals may be prepared in two ways: either by dissolving pure zirconium hydroxide in dilute hydrobromic acid and evaporating, with subsequent additions of 48 per cent. hydrobromic acid and repeated evaporation, or by saturating a concentrated solution of hydrogen bromide with zirconium hydroxide and evaporating.

Hinsberg (Abstr., 1887, 896) has described an oxyiodide, $\text{ZrI}(\text{OH})_3 + 3\text{H}_2\text{O}$. According to Melliss, an oxyiodide is not formed by dissolving the hydroxide in hydriodic acid, but the authors state that zirconium hydroxide, when precipitated cold, is soluble to a slight extent in strong, aqueous hydriodic acid; needles may be obtained on evaporation, but these are always contaminated with free iodine. When the hydroxide is treated with hydrogen iodide, a hard, horn-like, coloured mass is obtained which is insoluble in water or acids. J. J. S.

Zirconium Dioxide. By FRANCIS P. VENABLE and A. W. BELDEN (*J. Amer. Chem. Soc.*, 1898, 20, 273—276).—Carefully purified zirconium dioxide has a sp. gr. = 5.489, and after being strongly ignited is practically insoluble in all acids except hydrofluoric, in which it readily dissolves on heating; sodium zirconate, however, does not dissolve in hydrofluoric acid, probably owing to the formation of sodium zirconofluoride. Dilute sulphuric acid (sp. gr. = 1.56), when heated with powdered zirconia according to Berzelius's method, dissolves only 0.672 per cent. of its weight of the oxide. Contrary to Berzelius's statement, zirconia is not changed by prolonged heating with sodium carbonate; when strongly heated with microcosmic salt or with borax, it does not enter into fusion.

When the precipitate obtained by adding ammonia to a solution of a zirconium salt is pressed between filter papers and washed with light petroleum until a constant weight is attained, it approximates in composition to the hydroxide $\text{Zr}(\text{OH})_4$; when alcohol and ether are used in the washing, there appears to be no definite limit to the removal of water. Bruch's statement (*Jahresb.*, 1854, 729), that zirconium hydroxide is slightly soluble in water and has an alkaline reaction, is incorrect; the latter was probably due to the ammonia which zirconium hydroxide persistently retains. The hydroxide precipitated from a cold solution of a zirconium salt is easily soluble in either dilute or concentrated mineral acids, with the exception of hydriodic acid; in oxalic acid, it readily dissolves, but is only sparingly soluble in glacial acetic acid and saturated solutions of tartaric or citric acid; in saturated solutions of ammonium carbonate and ammonium tartrate, it is soluble to the extent of about 1 per cent. When precipitated from a hot solution, zirconium hydroxide dissolves much less readily in dilute mineral acids than when precipitated in the cold.

Basic carbonates, of widely varying composition, appear to be formed on passing carbonic anhydride over moist zirconium hydroxide.

W. A. D.

Compounds of Tervalent Vanadium. By JAMES LOCKE and GASTON H. EDWARDS (*Amer. Chem. J.*, 1898, 20, 594—606).—Vanadium trichloride appears to unite with potassium chloride to form a green, crystalline *double salt*, $KVCl_4$; it is doubtful, however, if this substance was obtained pure, since ferric chloride forms double salts of the type $2KCl, FeCl_3 + H_2O$.

Vanadium tribromide, $VBr_3 + 6H_2O$, prepared by dissolving vanadium hydroxide in pure, concentrated hydrobromic acid, is more unstable and crystallises less readily than the corresponding chloride.

Potassium vanadiocyanide, $K_3VC_6N_6$, prepared by adding an excess of potassium cyanide to an aqueous solution of vanadium chloride, and subsequently precipitating with alcohol, separates in bright scarlet, monosymmetric crystals, which are probably isomorphous with the corresponding derivatives of chromium, manganese, iron, cobalt, rhodium, and iridium; it is readily soluble in water, but is slowly decomposed by it, and immediately by mineral acids, hydrogen cyanide being evolved. The corresponding ammonium and sodium derivatives appear to exist only in solution. It is pointed out that the tendency of the metals, vanadium, chromium, manganese, iron, and cobalt, to form complex substances of the type $K_3MC_6N_6$, in preference to simple salts, diminishes as their atomic weight decreases.

Potassium vanadithiocyanate, $K_3V(CNS)_6 + 4H_2O$, prepared by adding a concentrated aqueous solution of vanadium chloride to somewhat more than the calculated quantity of alcoholic potassium thiocyanate, separates in very dark red crystals, and corresponds with the chromium salt, $K_3Cr(CNS)_6 + 6H_2O$; its aqueous solution rapidly decomposes, but is stable in presence of an excess of potassium thiocyanate, and only very slowly undergoes oxidation; alkalis precipitate vanadium hydroxide from the solution only on boiling, but acids cause immediate decomposition.

In order to avoid oxidation, all the compounds described were prepared in an atmosphere of hydrogen; a description is given of the apparatus employed.

W. A. D.

Bismuth Suboxide. By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1898, 31, 2267—2272. Compare this vol., i, 435).—The authors show that this oxide is never formed by the action of stannous chloride on bismuth chloride in alkaline solutions. If the bismuth chloride is in excess, the precipitate consists of a mixture of metallic bismuth with metahydroxide or oxychloride. Three molecular proportions of stannous chloride suffice to completely reduce bismuth oxide, Bi_2O_3 , to metallic bismuth. The behaviour of stannous chloride towards salts of bismuth is quite analogous to that of reducing agents such as hypophosphorous and hyposulphurous acids and formaldehyde, which also yield the metal, and not the suboxide.

G. T. M.

Hydrolytic Decomposition of Bismuth Nitrate. By UBALDO ANTONY and GUIDO GIGLI (*Gazzetta*, 1898, 28, i, 245—249).—On treating bismuth nitrate with varying quantities of water, the quantity of

bismuth going into solution decreases as the dilution increases, and a stage of dilution is at length reached when a precipitate of hydrate of bismuth containing no nitrate is thrown down, and the solution no longer contains any bismuth; at this stage, 1 part of bismuth nitrate is in contact with 50,000 parts of water. The authors have previously shown (Abstr., 1896, ii, 604) that when 1 mol. of ferric nitrate is in contact with 19,280,000 mols. of water, no iron remains in solution, and the present experiments show that no bismuth remains in solution if 1 mol. of bismuth nitrate is in contact with 19,605,000 mols. of water; the amounts of water required to effect this complete decomposition are in the ratio of 1:0.98 for the bismuth and ferric salts respectively, a result agreeing with the ordinary view, that the energy of an acid is independent of the nature of the associated base. W. J. P.

Purple of Cassius. By RICHARD ZSIGMONDY (*Annalen*, 1898, 301, 361—387).—The author describes experiments which afford fresh evidence in favour of Schneider's view regarding the soluble form of gold purple (Abstr., 1893, ii, 575). Contrary to this investigator, however, he does not regard the hydrosol of stannic acid as essential to the existence of the hydrosol of gold, it having been shown that a solution of gold is stable if it contains only a small proportion of acids or salts (this vol., ii, 522). Gold purple of required composition and shade may be obtained by mixing solutions of colloidal gold and colloidal stannic acid, and adding dilute acids or salt solutions.

An important outcome of the investigation is the recognition of the fact that a mixture of colloidal substances is capable of behaving like a chemical compound, the properties of either constituent of such a mixture being masked by those of the other.

From a mixture of the hydrosols of stannic acid and silver, dilute sulphuric acid precipitates a reddish-yellow substance; this dissolves in ammonia, and is also formed when silver nitrate is reduced in presence of stannic acid. M. O. F.

Occlusion of Oxygen and Hydrogen by Platinum Black.

By LUDWIG MOND, WILLIAM RAMSAY, and JOHN SHIELDS (*Proc. Roy. Soc.*, 1897, 62, 50—52. Compare Abstr., 1895, ii, 492).—Platinum black was saturated with hydrogen, heated at 184° under reduced pressure, then placed in an ice calorimeter and allowed to reabsorb the gas; it was found that 68.8 Cal. were developed per gram of hydrogen occluded. It is shown that the arguments put forward by Berthelot in favour of the existence of the compounds Pt_{30}H_2 and Pt_{30}H_3 are not justified, and that the difference observed by Favre between the behaviour of palladium and platinum towards hydrogen was merely due to the presence of oxygen in the platinum black.

Attempts made to remove oxygen from platinum black, with a view to the determination of its heat of occlusion, showed that reducing agents, whilst eliminating the oxygen from the substance, were themselves occluded and obstinately retained. It was also found that hydrogen, admitted to platinum black, does not remove all the oxygen, but only replaces that first removed, both gases being therefore occluded simultaneously.

Platinum black, saturated with hydrogen, was exhausted at 184°,

and then allowed to come into contact with small quantities of oxygen. It was found that, after a certain point, the addition of more oxygen caused the pressure to increase; a further small quantity of gas was absorbed, however, on adding oxygen up to atmospheric pressure, and the heat simultaneously developed represented the true heat of occlusion of this quantity of oxygen. The results thus obtained were in close agreement with others obtained by an indirect method, and, as a mean, the value found was 11.0 Cal. per gram of oxygen occluded. This number is almost identical with that given by Thomsen for the heat of formation of platinous hydroxide; this suggests the possibility that the two phenomena may be identical, the water necessary being present in platinum black dried in a vacuum. A. L.

Occlusion of Hydrogen and Oxygen by Palladium. By LUDWIG MOND, WILLIAM RAMSAY, and JOHN SHIELDS (*Proc. Roy. Soc.*, 1897, 62, 290—293. Compare preceding abstract).—Palladium black, prepared in the same way as platinum black, contains 1.65 per cent. of oxygen, or, taking the density of palladium black as 12.0, 138 volumes of oxygen. Unlike the oxygen in platinum black, however, it cannot be removed at a dull red heat in a vacuum, but must be removed by ignition in a stream of hydrogen. Palladium black, dried at 100°, contains 0.72 per cent. of water, and assuming that the oxygen exists as PdO, the composition of the substance is Pd = 86.59; PdO = 12.69; H₂O = 0.72 per cent.

Palladium black absorbs oxygen when heated in it, at least up to a red heat, and yields a brownish-black substance which does not lose its oxygen at a red heat in a vacuum; the amount absorbed is nearly 1000 volumes, or about three-fourths of that required for the complete formation of the oxide PdO.

Palladium black was found to absorb over 1000 volumes of hydrogen, of which only 873 are occluded, the rest having formed water with the oxygen originally present. About 92 per cent. of the occluded gas was slowly pumped off at the ordinary temperature, and most of the remainder at 444°. Increase of the pressure of the hydrogen from 1 atmosphere to 4.6 had no influence on the quantity absorbed at the ordinary temperature. The pure palladium sponge remaining after the foregoing experiment occluded 852 volumes of hydrogen, and of this 98 per cent. was extracted in a vacuum at the ordinary temperature.

New palladium foil refused to occlude hydrogen after ignition in the gas, and even after repeated charging and discharging with the gas electrolytically. After powerful ignition on the blowpipe flame, however, when it was probably alternately oxidised and deoxidised, it was finally induced to absorb hydrogen to the extent of 846 volumes, or about the same amount as the black or sponge. The hydrogen thus occluded is slowly given off in a vacuum at the ordinary temperature, and rapidly and almost completely at 100°.

The heat of occlusion of hydrogen by palladium black was measured in nearly the same way as in the case of platinum black (see preceding abstract). Favre's statement that the heat of occlusion remains constant for different fractions of hydrogen was confirmed, and it was

found that +46.4 Cal. was developed per gram of hydrogen occluded, or if the work done by the atmosphere be allowed for, the value becomes 43.7 Cal.

The heat developed per gram of oxygen absorbed was also determined in an indirect manner and found to be +11.2 Cal. This number, referred to 16 grams of oxygen, is intermediate between the values found by Thomsen for the heat of formation of palladious and palladic hydroxides, and may be consistent with the formation of either or both of these substances; this fact, taken in conjunction with the similar results obtained in the case of platinum black, favours the view that the occlusion of oxygen by palladium and platinum is a true oxidation phenomenon.

From the investigation of the atomic ratio of palladium to hydrogen in the fully charged metal, the authors conclude that the amount of hydrogen absorbed is independent of the form of the metal, and that the atomic ratio varies between 1.37 and 1.47.

Hoitsema has shown that Troost and Hautefeuille's supposition, that a compound of the formula Pd_2H is formed, is not warranted. The composition of fully charged palladium hydrogen corresponds closely with the formula Pd_3H_2 suggested by Dewar, but is almost the only evidence in favour of the existence of such a definite chemical compound.

The results do not favour the view that the heat of occlusion of a gas represents the heat of condensation or liquefaction, or of the heat of solidification or fusion.

A. L.

Mineralogical Chemistry.

Mineral Intergrowths. By ARVID G. HÖGBOM (*Bull. Geol. Inst. Univ. Upsala*, 1898, 3, 433—453).—Cases of intergrowth of various minerals are described; namely, of quartz and felspar, beryl and felspar, quartz and muscovite, quartz and tourmaline, quartz and calcite, leucite and mica. Only in a few cases is there any definite crystallographic orientation of the two minerals with respect to each other. In the case of leucite and mica (in lava from Frascati, near Rome), a large plate of bronze mica encloses numerous grains of leucite, the structure of the whole being poecilitic. The grains of leucite have sharp crystal outlines, but, under the microscope, they are seen to be built up of several differently orientated individuals with a stronger birefringence than ordinary leucite. Analysis of this pseudo-leucite gave,

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.
58.20	24.28	1.74	0.50	trace	11.32	0.93	2.85	99.82

This differs from fresh leucite in containing considerably less potash, which has possibly been partly replaced by water. Iron is due to inclosed impurities.

L. J. S.

Native Lead and Copper from Franklin Furnace, New Jersey. By WARREN M. FOOTE (*Amer. J. Sci.*, 1898, [iv], 6, 187—188).—Small quantities of native lead have recently been found at Franklin Furnace, New Jersey, in association with native copper, garnet, axinite, &c., and also with røblingite (Abstr., 1897, ii, 563) and another silicate containing lead. This association of native lead with silicates of lead is well known from Sweden. L. J. S.

Constitution of Arsenopyrite [= Mispickel]. By F. W. STARKE, H. L. SHOCK, and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1897, 19, 948—952. Compare Abstr., 1895, ii, 17, 316).—Mispickel (FeAsS) has been considered as iron sulphide (FeS_2) with the sulphur partly replaced by As'', or as iron arsenide (FeAs_2) containing S'''. In attempting to determine the true constitution of the mineral, the following experiments were made.

When heated in hydrogen, all the sulphur is expelled as hydrogen sulphide, whilst the iron and practically all the arsenic remain; this indicates that the sulphur is less intimately combined with the iron than is the arsenic. Pyrites and marcasite lose half their sulphur when heated in hydrogen.

Heating with ammonium chloride in nitrogen, and dissolving in water, gave indications of the presence of much ferrous, but only a little ferric, iron.

Heating with copper sulphate solution in sealed tubes and titrating with permanganate showed the presence of much ferrous iron and arsenious acid.

Heating in a current of dry hydrogen bromide showed the presence of about 28 per cent. of ferrous iron, and in dry hydrogen chloride of 30·86, 30·55, 30·16 per cent. Since there is 34·35 per cent. of iron in mispickel, this leaves about 4 per cent. for ferric iron.

The formula of mispickel is therefore given provisionally as $14\text{Fe}''\text{As}''\text{S}, 2\text{Fe}'''\text{As}''\text{S}$. Experiments to determine the molecular weight by observing the influence of mispickel on the solidification point of alloys were without result. No differences in the specific heat and electrical conductivity of pyrites and marcasite respectively could be detected. L. J. S.

[Magnetite and Pyrrhotite]. By G. NYIREDY (*Zeit. Kryst. Min.*, 1898, 30, 184; from *Értessítő az erd. Múzeum egyl. orv.-term.-tud. szakosztályából.*, 1896, 21, 123—128, 29—31. Compare Abstr., 1896, ii, 657). I. mean for massive magnetite from Vaskő; sp. gr. 4·696. II. Pyrrhotite from Borév; III. from Ó-Radna; IV. from Oravicza.

	SiO_2 .	Fe.	O.	S.	Total.
I.	5·72	68·10	25·93	—	99·75
II.	4·42	57·68	—	37·66	99·76
III.	4·92	57·30	—	37·42	99·64
IV.	7·25	55·92	—	36·48	99·65

L. J. S.

Krennerite from Cripple Creek, Colorado. By ALBERT H. CHESTER (*Amer. J. Sci.*, 1898, [iv], 5, 375—377).—The rare mineral krennerite has previously only been known from Nagyag; it is now

described as bright crystals, associated with quartz and pyrites, from the Independence mine at Cripple Creek. The colour is pale yellowish-bronze, but on the perfect basal cleavage it is tin-white. The mineral is very brittle; $H = 2.5$. When heated, it decrepitates. Measurements of the orthorhombic crystals are given by S. L. Penfield. Analysis of crystals by W. S. Myers gave results agreeing with the formula $AuTe_2$.

Au.	Ag.	Fe_2O_3 .	Insol.	Te.	Total.
43.33	0.45	trace	1.21	[55.01]	100.00

This composition is very close to that of the calaverite from Cripple Creek analysed by Hillebrand, and determined by Penfield to be possibly anorthic (Abstr., 1896, ii, 31). There therefore seems to be three tellurides of gold and silver with the formula $(Au,Ag)Te_2$, namely, the orthorhombic krennerite, the monosymmetric sylvanite, and the anorthic (?) calaverite, although the last two may possibly be identical, only differing in the amount of silver present.

L. J. S.

A New Copper Antimonide. By CARL HLAUWATSCH (*Ber. Akad. Wien*, 1895, 104, i, 275—296).—A crystallised product obtained in the process of smelting tetrahedrite at Brixlegg, Tyrol, is described. After deducting about 10 per cent. of metallic lead, which is enclosed in the crystal plates, analysis gave the formula Cu_2Sb . The crystals are orthorhombic; they are very brittle, and have a violet colour with metallic lustre; sp. gr. = 8.389. The same kind of crystals, but with the formula Cu_3Sb_5 , are obtained by melting together copper and antimony; the difference in composition may be due to the presence of metallic antimony in the latter crystals, or the composition may vary without affecting the crystalline form, as in dyscrasite.

L. J. S.

Nickeliferous Opal from Tamworth, New South Wales. By DONALD A. PORTER (*Proc. Roy. Soc. N.S.W.*, 1898 [for 1897], 31, p. xxviii).—Green opal occurs with pinkish chaledony as thin veins in serpentine in the "Never-never" ranges, near Tamworth, Co. Inglis, N.S.W. It is translucent to opaque, and of a pale to deep apple-green colour. The darker coloured material gives a strong nickel reaction.

L. J. S.

Origin of Corundum in North Carolina. By JULIUS H. PRATT (*Amer. J. Sci.*, 1898, [iv], 6, 49—65).—Although the corundum of the extensive deposits in North Carolina is rarely found actually in the peridotites (dunite) and serpentines, which are intrusive in the gneiss, the author deduces from field evidence that these peridotites are the mother rock of the corundum. That corundum is capable of crystallising from such a magma, and so can be of igneous origin, has been shown by Morozewicz and by Lagorio (Abstr., 1895, ii, 275 and 276).

L. J. S.

Minerals of the Island San Pietro, Sardinia. By SOLIMANN BERTOLIO (*Zeit. Kryst. Min.*, 1898, 30, 201—202; from *Boll. R. Com. Geol. Italia*, 1896, 27, 405—421).—The principal minerals of this

locality are feldspar (anorthoclase, oligoclase, labradorite), quartz, opal, tridymite, amphibole (arfvedsonite), barytes, and pyrolusite (compare this vol., ii, 81). Analysis of non-crystalline pyrolusite gave,

MnO ₂ .	MnO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	P ₂ O ₅ .	SiO ₂ .	SO ₃ .	Comb. H ₂ O. at 100°.	Loss. Total.
36.0	4.0	15.0	5.0	1.0	2.0	0.4	9.1	0.1	6.3	20.5 99.4

It appears to have been deposited from spring-water containing manganese carbonate in solution.

L. J. S.

Ktypeite, a New Form of Calcium Carbonate. By ALFRED LACROIX (*Compt. rend.*, 1898, 126, 602—605).—The pisolites formed in the hot springs of Carlsbad (Bohemia) and Hamman-Meskoutine (Constantine), are usually considered to consist of aragonite, but the author finds that the optical characters agree with neither those of aragonite nor of calcite. Thin sections show, in parallel polarised light, a distorted, black cross, and portions which are dark between crossed nicols give a positive black cross in convergent light; in the material from Hamman-Meskoutine the apparent angle of the optic axes is 50°. The birefringence, about 0.020, is much less than in the optically negative calcite and aragonite, and consequently bright polarisation colours are seen. When heated to low redness, the pisolites violently decrepitate, and detached scales are then observed to be partly transformed into calcite. If a ball be first cracked and gently heated for some time, it becomes completely transformed into calcite without breaking up. The sp. gr., 2.58—2.70, varies, possibly owing to enclosed cryptocrystalline aragonite and to porosity, but is always less than that of calcite (2.72) [previous observers have found it to be near that of aragonite (2.93)]. The violent decrepitation, on account of which the name ktypeite is given, shows that the pisolites must be in a state of considerable strain, and this may possibly explain the optical anomalies observed.

L. J. S.

Aurichalcite from Tuscany. By GIOVANNI D'ACHIARDI (*Jahrb. f. Min.*, 1898, i, Ref., 439; from *Atti Soc. Toscana Sci. Nat.*, 1897, Mem., 16, 15 pp.).—The small crystals obtained on crushing a crystalline mass of aurichalcite from Campligia Marittima, are shown by microscopical examination to be monosymmetric, with $b:c = 1:1.6574$; $\beta = 84^\circ 15'$. There is a distinct cleavage parallel to (100); the optical characters, so far as determined, are given. Aurichalcite (so-called "buratite"), from Valdaspra, gave the same results; this has sp. gr. = 3.00—3.02, and gave, on analysis,

H ₂ O.	CO ₂ .	ZnO.	CuO.	CaO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	Insol.	Total.
9.61	15.71	52.51	18.80	0.45	1.34	trace	2.01	100.43

Formula, $2(\text{Zn,Cu})\text{CO}_3, 3(\text{Zn,Cu})(\text{OH})_2$, with Cu:Zn = 2:5.

L. J. S.

Apatite in Granulitic Enclosures in the Puy de Dôme. By A. GONNARD and ADELPHÉ (*Compt. rend.*, 1898, 126, 1532—1534).—Enclosures of apatite in volcanic rocks are comparatively rare, but the authors have found chocolate-coloured, hexagonal prisms of this mineral 3 mm. broad and 12 mm. long in a deep brown quartzose

mass, and in nodules of an altered white felspar at Chuquet-Genestoux in the Puy de Dôme. Several of the crystals are traversed by a small, central cylindrical canal, possibly filled originally with muscovite that has since disappeared. The apatite contains somewhat considerable quantities of iron, doubtless derived from the volcanic rocks in which it occurs.

C. H. B.

[Ferric Sulphate from Minnesota]. By CHARLES P. BERKEY (*Amer. Geologist*, 1898, 21, 153).—In a paper on the geology of St. Croix Dalles, the following analysis, by H. A. Webber, is given of greenish-yellow, rather compact, globular masses, which are abundantly formed as an efflorescence on exposed pyritiferous shales at Taylor's Falls.

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	K ₂ O.	Na ₂ O.	CaO.	SO ₃ .	H ₂ O.	Organic matter.	Total.
12·946	22·828	4·141	1·844	4·659	2·210	32·500	17·840	trace	98·968

As shown by the presence of silica, the substance is apparently a mixture.

L. J. S.

Orthoclase as Gangue Mineral in a Fissure Vein. By WALDEMAR LINDGREN (*Amer. J. Sci.*, 1898, [iv], 5, 418—420).—Felspars as a gangue material in ordinary fissure veins are not common; there are several recorded occurrences of orthoclase and albite in gold-quartz and other veins, but anorthite and soda-lime felspars are very rare. A vein on Florida Mountain, in the Silver City mining district of southern Idaho, contains pyrites, copper pyrites, and argentite, with a gangue of quartz and orthoclase. The vein is richest in orthoclase where it traverses granite, there is less where it intersects rhyolite, and none where it intersects basalt. The orthoclase occurs as large, irregular, milk-white grains intergrown with vein-quartz, and enclosing pyrites and argentite, or as crystals coating quartz and lining crevices in the altered granite adjoining the vein. The crystals are of the adularia habit with the forms $m\{110\}$ and $x\{101\}$. Analysis of a crystal by Hillebrand gave,

SiO ₂ .	Al ₂ O ₃ .	K ₂ O.	Na ₂ O.	Undet.	Total.	Sp. gr.
66·28	17·93	15·12	0·25	0·42	100·00	2·54

Orthoclase has been formed artificially in the wet way, and this supports the idea that the vein orthoclase has been formed by aqueous deposition. Why it is not of more common occurrence may possibly be due to the frequent presence of carbonated thermal waters in mineral veins.

L. J. S.

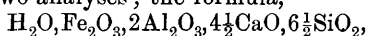
Rhodolite, a New Variety of Garnet. By WILLIAM E. HIDDEN and JULIUS H. PRATT (*Amer. J. Sci.*, 1898, [iv], 5, 294—296).—A “rose garnet,” named rhodolite on account of its rose-red or rhododendron-red colour, occurs as rolled pebbles in the gravels of a brook called Mason's Branch, in Macon Co., North Carolina. Associated with it are quartz (rarely pseudomorphous rhombic dodecahedra), pyrope, corundum of various colours, spinel, bronzite, cordierite, kyanite, fibrolite, hornblende, staurolite, rutile, ilmenite, chromite, monazite, zircon, gold, and sperrylite. This garnet is unusually free

from internal flaws and inclusions, and forms a fine gem-stone which in brilliancy resembles the green demantoid from the Urals. Sp. gr. = 3·837; analysis gave,

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Total.
41·59	23·13	1·90	15·55	17·23	0·92	100·32

This agrees closely with the formula $2\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3, \text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$; that is, two molecules of pyrope with one of almandine. L. J. S.

Epidote, &c., from Oulx. By LUIGI COLOMBA (*Zeit. Kryst. Min.*, 1898, 30, 203—204; from *Atti R. Accad. Sci. Torino*, 1891, 26, 811—826).—*Epidote*.—The larger crystals are dark olive-green, opaque, and deeply striated, whilst the smaller are light in colour, transparent, and with smooth faces. A list of the observed crystal forms is given. I is the mean of two analyses; the formula,



indicates that the material was not pure.

Actinolite.—Analysis of pure material gave the results under II. With this amphibole is mixed a brownish-yellow mineral which gave analysis III; it appears to be a decomposition product of epidote and amphibole.

Albite.—This is often green, owing to enclosed epidote. IV is the mean of two analyses. A crystallographic description is given.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Loss on ignition.	Total.
I.	37·48	20·39	15·30	—	23·99	0·48	1·89	99·53
II.	54·65	0·47	—	10·37	16·13	18·68	—	100·30
III.	46·17	8·03	10·51		22·63	12·92	Na ₂ O K ₂ O	100·26
IV.	67·66	17·03	0·75	—	3·79	0·14	9·16 0·85	99·38

Calcite, quartz, hæmatite, and pyrites are also described from this locality, which is situated in the upper valley of the Dora Riparia, Piedmont. L. J. S.

Anthophyllite, Enstatite, and Emerald from North Carolina. By JULIUS H. PRATT (*Amer. J. Sci.*, 1898, [iv], 5, 429—432).—*Anthophyllite*.—Boulders found on the surface of an outcrop of dunite near Bakersville, in Mitchell Co., North Carolina, contain prismatic crystals of anthophyllite embedded in penninite; the least altered are transparent, and pale clove-brown to flesh-red in colour, and show the forms {110} and {010}; analysis I. Fibrous anthophyllite also occurs at Corundum Hill, in Macon Co., but that described by Penfield (*Abstr.*, 1891, 529) as being from this locality is probably from Bakersville.

Enstatite.—The enstatite from Corundum Hill, in Macon Co., which is commonly called anthophyllite, occurs as a tough rock, continuous with the dunite, composed of a mass of interlocking, bladed, greyish crystals. Analysis II shows it to be impure, and to be composed of enstatite, 44·5; serpentine, 35; and talc, 20·5 per cent.

Enstatite (Bronzite).—A bronzite-diopside rock (websterite) occurs in the midst of dunite near Webster, in Jackson Co. The bronzite has a resinous-brown colour with a bronze-like lustre, and the interlocking crystals form a very tough rock. Analysis III gives

the formula $(\text{Mg}, \text{Fe})\text{O}, \text{SiO}_2$, with $\text{Mg} : \text{Fe} = 7 : 1$ (Anal. I—III by Baskerville).

	SiO_2 .	Al_2O_3 .	Cr_2O_3 .	FeO .	MnO .	MgO .	CaO .	H_2O .	Total.
I.	56.40	1.15	—	11.40	—	28.68	0.50	1.63	99.76
II.	51.64	0.12	—	9.28	0.56	31.93	0.45	5.45	99.43
III.	53.62	0.97	0.50	9.06	—	33.53	1.75	0.19	99.62

Beryl (Emerald).—Beryl is common in granite veins, but the emerald-green variety is rare; the latter is found in a pegmatite vein, composed of quartz and albite with accessory tourmaline and garnet, in the gneisses and schists of Mitchell Co. L. J. S.

Clinohedrite: A New Mineral from Franklin, New Jersey. By SAMUEL L. PENFIELD and H. W. FOOTE (*Amer. J. Sci.*, 1898, [iv], 5, 289—293).—The new mineral is from the Trotter Mine at Franklin, New Jersey, where it is associated with willemite, garnet, phlogopite, axinite, and datolite. The monosymmetric crystals are interesting on account of their hemihedrism, there being a plane of symmetry, but no axis of symmetry (domatic class of Groth); owing to the absence of parallel faces (except $b(010)$), the crystals present a peculiar inclined-faced character, hence the name clinohedrite. $a : b : c = 0.6826 : 1 : 0.3226$; $\beta = 76^\circ 4'$. There is a perfect cleavage parallel to $b(010)$. $H = 5.5$; sp. gr. = 3.33. The crystals are pyroelectric; they are often transparent, and the colour varies from amythestine to nearly colourless or white. The optic axial plane and the obtuse bisectrix are perpendicular to $b(010)$; the birefringence is negative and not very strong. The mean of two analyses is

SiO_2 .	ZnO .	MnO .	CaO .	MgO .	H_2O .	$(\text{Fe}, \text{Al})_2\text{O}_3$	Total.
27.22	37.44	0.50	26.25	0.07	8.56	0.28	100.32

This agrees closely with $\text{H}_2\text{ZnCaSiO}_5$, or, as the water is not expelled much below a faint red heat, $\text{SiO}_3(\text{ZnOH})(\text{CaOH})$. This formula is analogous to that of hemimorphite, $\text{H}_2\text{Zn}_2\text{SiO}_5$, or $\text{SiO}_3(\text{ZnOH})_2$. [The name clinohedrite is preoccupied.] L. J. S.

Mineralogical Notes. By C. H. WARREN (*Amer. J. Sci.*, 1898, [iv], 6, 116—124).—(1) *Melanotekite from New Mexico.*—This mineral, previously only known from Sweden, has recently been found at Hillsboro, associated with cerussite and a brown, jasper-like material; it has a dark-brown to almost black colour, and gives an ochre-yellow streak resembling that of limonite. Cavities are lined with minute orthorhombic crystals of prismatic habit; $a : b : c = 0.6338 : 1 : 0.9126$. The mean of two very close analyses is,

SiO_2 .	PbO .	Fe_2O_3 .	X.	H_2O .	Total.	Sp. gr.
15.49	55.56	27.51	0.82	0.68	100.06	5.854

This agrees closely with the formula $2\text{Fe}_2\text{O}_3, 3\text{PbO}, 3\text{SiO}_2$, or, written as a basic salt of orthosilicic acid, $(\text{Fe}_2\text{O}_3)_3\text{Pb}_3(\text{SiO}_4)_3$, the radicle, Fe_4O_3 being hexavalent as in limonite, $\text{Fe}_4\text{O}_3(\text{OH})_6$. The formula previously given for melanotekite is $2\text{PbO}, \text{Fe}_2\text{O}_3, 2\text{SiO}_2$, and for the isomorphous kentrolite, $2\text{PbO}, \text{Mn}_2\text{O}_3, 2\text{SiO}_2$. The four earlier analyses of these two minerals show considerable variations, and three of them agree better with the new formula than with the old.

(2) *Pseudomorphs after phenakite from Greenwood, Maine.*—These are large, whitish crystals, up to 12 in. diam., and weighing 28 lbs., with rough, pitted surfaces; they are of unusual habit, but measurements show the presence of the characteristic forms and symmetry of phenakite. In thin sections, they are seen to consist of quartz and a micaceous mineral, which, as seen from the following analysis, is probably cookeite.

Al_2O_3 .	Fe_2O_3 .	BeO .	Li_2O .	Na_2O .	K_2O .	H_2O .	SiO_2 .	Total.
19.30	0.54	Nil	0.68	1.17	0.67	5.53	[72.11]	100.00

(3) *Supposed pseudomorphs after topaz from Greenwood, Maine.*—Hollow, prismatic shells of quartz, lined with small crystals of quartz and rounded prominences of cookeite, show the topaz forms $m\{110\}$ and $c\{001\}$.

(4) *Crystallised Tapiolite from Topsham, Maine.*—This occurs in the felspar quarries at Topsham as simple and twinned tetragonal crystals, 2 cm. diam.; the twinned crystals have the same orthorhombic habit as recently described by Brögger (this vol., ii, 388). The high sp. gr., 7.66–7.87, of the crystals indicate that they are tapiolite (FeTa_2O_6) rather than mossite (FeNb_2O_6). Only a trace of manganese is present.

(5) *Crystallised Tantalite from Paris, Maine.*—The crystals are orthorhombic, with forms corresponding to those of columbite (FeNb_2O_6), but the high sp. gr., 7.26, indicates that they are tantalite (FeTa_2O_6). It differs from the tantalites previously described in containing little or no manganese.

(6) *Cobaltiferous Calamine from Boleo, Lower California.*—This occurs as small, crystalline particles, of a delicate pink colour, embedded in gypsum, and associated with atacamite; sp. gr. = 3.874. The mean of two analyses is,

CO_2 .	FeO .	ZnO .	CoO .	MnO .	MgO .	CuO .	Cl .	H_2O .	Total.
36.94	0.33	39.02	10.25	3.36	7.22	1.65	0.11	1.29	100.17

Deducting CuO , H_2O , and Cl as atacamite, this gives the formula RCO_3 . L. J. S.

Erionite, a New Zeolite. By ARTHUR S. EAKLE (*Amer. J. Sci.*, 1898, [iv], 6, 66–68, and *Zeit. Kryst. Min.*, 1898, 30, 176–178).—This zeolite occurs in a rhyolite-tuff at Durkee, Oregon, as white tufts on opal, or as compactly matted fibres filling rock fissures. The very delicate threads, resembling fine, woolly hairs, are snow-white, and have a pearly lustre; sometimes they are coated with a thin shell of white opal. The optical characters point to orthorhombic symmetry, there being an acute positive bisectrix parallel to the length of the fibres. Sp. gr. = 1.997. The mineral, when heated, emits an odour of burning, gives off water of alkaline reaction, and easily fuses to a clear, colourless glass. Over sulphuric acid, there is a loss of 6.95, at 110° of 7.68, and at 280° of 15.25 per cent., this being regained from moist air; up to 400° , there is no further loss, the remainder going off only at a low, red heat. Alkaline water is still given off at 200° , but not at 280° ; the amount of ammonia in the mineral is 0.22 per cent. The

organic matter cannot be extracted by boiling water or acids. The fibres are soluble with great difficulty in hydrochloric acid, with separation of pulverulent silica. The mean of three analyses is,

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
57·16	16·08	3·50	0·66	3·51	2·47	17·30	100·68

Formula, $6\text{SiO}_2, \text{Al}_2\text{O}_3, (\text{Ca}, \text{K}_2, \text{Na}_2)\text{O} + 6\text{H}_2\text{O}$, or $\text{H}_2\text{Si}_6\text{Al}_2(\text{Ca}, \text{K}_2, \text{Na}_2)\text{O}_{17} + 5\text{H}_2\text{O}$. This is the formula of stilbite, with lime largely replaced by alkalis; the physical characters are, however, distinct from those of stilbite, and the new name, *erionite*, is given on account of the woolly nature.

Opal occurs as large masses filling cavities in the tuff, and it sometimes shows a rich play of colours; analysis of the more common milk-opal gave SiO₂, 95·56; Al₂O₃, trace; H₂O, 4·14 per cent.

L. J. S.

Barium-Heulandite and other Zeolites from Sardinia. By DOMENICO LOVISATO (*Jahrb. f. Min.*, 1898, i, Ref. 446—447; from *Rend. R. Accad. Lincei*, 1897, 6, i, 260—264, and *Riv. Min. Crist. Ital.*, 1898, 18, 33—38).—Zeolites are of comparatively rare occurrence in Sardinia; the volcanic rocks contain heulandite, stilbite, chabazite, and analcite, and the mineral veins, laumontite and harmotome. Cavities in hornblende-andesite at Cape Pula are encrusted with a pale rose-coloured, transparent heulandite; the crystals show the forms {110}, {100}, {001}; sp. gr. = 2·182; analysis gave,

SiO ₂ .	Al ₂ O ₃ .	BaO.	CaO.	Na ₂ O.	H ₂ O.	Total.
56·67	16·86	2·55	3·61	3·27	17·05	100·01

This may, then, be called barium-heulandite. The same mineral also occurs in trachytic and andesitic rocks in the mountains of Monastir, but not in the basaltic rocks, which contain stilbite. Notes are added on the occurrence, &c., of the other zeolites mentioned above.

L. J. S.

Epidote from Piedmont. By GIOVANNI BOERIS (*Jahrb. f. Min.*, 1898, i, Ref. 443; from *Atti R. Accad. Sci. Torino*, 1897, 32, 670—680, and *Riv. Min. Crist. Ital.*, 1898, 20, 65—76).—At the junction of the green schists and the serpentine schists of the Comba di Compare Robert, near Avigliana in the Piedmontese Alps, there is found here and there a crystalline aggregate of epidote, chlorite, sphene, and garnet. On the walls of calcite veins are good crystals of epidote, garnet, and diopside; crystallographic descriptions are given of these minerals. The epidote gave $2V_{Na} = 76^\circ 1'$, $\rho > v$, &c. (compare *Abstr.*, 1896, ii, 371); sp. gr. = 3·462. Analysis gave,

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O.	Total.
37·73	21·11	16·22	0·32	22·55	trace	99·91

Formula, $\text{H}_2\text{O}, 4\text{CaO}, 2\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, 6\text{SiO}_2$.

L. J. S.

Minerals of a Volcanic Vent in the Puy de Dôme. By ALFRED LACROIX and PAUL GAUTIER (*Compt. rend.*, 1898, 126, 1529—1532).—The authors describe in detail the minerals, and more particularly the crystallised silicates, found in an ancient volcanic vent at Royat, in the Puy de Dôme. The projected matter consists of fine ashes and

porous, basaltic lapilli, enclosing large numbers of fragments of granite, arkose, orthoclase, and quartz, all more or less fused. The crystallised silicates are unusually abundant, doubtless owing to the action of the gases in the vent, and they include pyroxene in several varieties, biotite, augite, labradorite, andesine, and albite, or anorthite, together with specular hæmatite and magnetite. It is probable that they were formed by the action of the gases on granitic enclosures which had been fused to vesicular glasses.

C. H. B.

"Mineral Soap." By WILBUR C. KNIGHT (*Engineering and Mining Journal* (New York), 1897, 63, 600—601).—In many parts of Wyoming, the Fort Benton (Cretaceous) shales contain a bed of peculiar clay, which is extensively worked at Rock Creek, Albany Co. It has an unctuous feel, and, on exposure, changes in colour from greenish-yellow to light cream. Sp. gr. = 2.132. With it are associated thin bands of secondary gypsum and mirabilite. The extremes of four partial analyses, made on material from different counties, are,

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	CaO.	Na ₂ O.	SO ₃ .	H ₂ O.
59.78	12.62	2.40	1.82	0.73	—	0.88	9.17
65.24	17.12	3.70	4.14	4.12	0.20	1.53	16.26

For this clay, the name taylorite is proposed [a name already in use].

L. J. S.

Rocks and Minerals from California. By HENRY W. TURNER (*Amer. J. Sci.*, 1898, [iv], 5, 421—428).—(1) A peculiar quartz-amphibole-diorite.—This occurs as a dyke-like streak in granite-diorite on the dividing ridge between Butte and Plumas counties; it is a greyish-green rock of medium grain, composed of amphibole, plagioclase (oligoclase or andesine), and quartz with accessory rutile, zircon, apatite, and magnetite, and secondary epidote, chlorite, and sericite. Analysis by Hillebrand is given under I (traces of Li₂O and P₂O₅ are also present). The abundant greyish-green amphibole occurs as short, idiomorphic needles enclosed in feldspar and quartz; extinction angle, 23°. Analysis II, by Valentine, shows that it contains too much alumina to be called actinolite.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO.	MnO.	NiO.	CaO.	SrO.	BaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	54.64	0.61	12.09	1.81	5.03	0.13	0.05	7.74	trace	0.05	11.36	1.01	2.35	2.56	100.01
II.	50.08	0.76	8.13	2.69	6.71	0.49	—	11.21	Nil	—	16.31	0.46	1.22	1.40	99.46

(2) A new amphibole-pyroxene rock from Mariposa Co.—This occurs as small, probably intrusive, masses in slate, and consists of grains of original amphibole and augite with a little quartz and some pyrrhotite. Large phenocrysts of amphibole enclose grains of augite, pyrrhotite, and amphibole similar to those in the ground-mass.

(3) A quartz-alunite rock.—Three sharp buttes called Tres Cerritos, in Mariposa Co., are composed of augite-porphyrity-tuffs and clay-slate which have been subjected to solfataric action. Most of the altered rocks are light brown, highly siliceous, and resemble quartzite in appearance; under the microscope, they are seen to consist of quartz with a mineral which is shown, by the following analysis, made by Valentine on

material separated by a heavy liquid, to be alunite; sp. gr. = 2.78; also traces of MgO and P_2O_5 .

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	SO ₃ .	Total.
2.64	0.40	38.05	0.23	0.55	4.48	2.78	11.92	38.50	99.55

(4) Zircons from gravels.—Small crystals of zircon have been isolated from the heavy sands obtained in the gravel washings at Eagle Gulch, Plumas Co.

(5) Molybdenite.—Three new occurrences are noted.

(6) Tellurium, selenium, and nickel in gold ores.—Tellurium has long been known to occur in various Californian gold ores; new localities of such occurrences are here given.

(7) Carbonaceous material in quartz.—Many veins in the Gold Belt region of the Sierra Nevada are composed of a dark quartz containing very finely disseminated colouring matter. Eight grams of this quartz dissolved in hydrogen fluoride left several milligrams of carbonaceous residue.

(8) Berthierite.—An ore containing iron, antimony, sulphur, &c., is recorded doubtfully as berthierite, but is more probably a mixture.

L. J. S.

Sölvbergite and Tinguaita from Essex Co., Mass. By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1898, [iv], 6, 176—187).—The igneous rocks of Essex Co., Massachusetts, are analogous to those of the Christiania region described by Brögger. Glaucophane-sölvbergite, occurring as dykes in granite at Cape Ann, is a dark, fine-grained rock of sp. gr. = 2.703. Under the microscope, it is seen to be holocrystalline with microgranitic structure, and to be composed of glaucophane-riebeckite (24.4 per cent., as calculated from the analysis I of the rock), albite (39.0), orthoclase (29.8), quartz (4.3), with accessory sphene, cordierite, and apatite. The hornblende is strongly pleochroic, and has an extinction angle of 4—7°; as calculated from the rock analysis, it is a mixture of ferrous-glaucophane and riebeckite in the ratio of 3:2.

From analysis II, of soda-granite from Quincy, Mass., is calculated the following mineralogical composition: riebeckite-glaucophane ($Rb_9Gl_2 = 14.3$ per cent.), albite (27.7), orthoclase (27.2), quartz (30.2). This is compared with Brögger's grorudite from Norway.

Analcite-tinguite, occurring as dykes in granite near Manchester, is a dark, very compact rock of sp. gr. = 2.474. Needles and grains of aegirite (10.2 per cent., as calculated from analysis III of the rock) and phenocrysts of feldspar (albite, 20.9; orthoclase, 17.3) lie in a clear, colourless ground of analcite (37.4) and nephelite (10.9). Dilute hydrochloric acid dissolves 49.24 per cent. of the rock.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	P ₂ O ₅ .	Total.
I.	64.28	0.50	15.97	2.91	3.18	trace	0.03	0.85	7.28	5.07	0.20	0.08	100.33
II.	73.93	0.18	12.29	2.91	1.55	trace	0.04	0.31	4.66	4.63	0.41	—	100.91
III.	56.75	0.30	20.69	3.52	0.59	trace	0.11	0.37	11.45	2.90	3.22	}	99.92
SO ₃ trace, Cl 0.28													

L. J. S.

Weathering of Diabase in Virginia. By THOMAS L. WATSON (*Amer. Geologist*, 1898, **22**, 85—101. Compare Abstr., 1897, ii, 107).—Olivine-dyabase occurs as dykes intersecting the crystalline schists near Chatham, Pittsylvania Co., Virginia; it shows various stages of decay, and the final product is a tough, bright red clay with embedded boulders. The large pleochroic crystals of augite extracted from the fresh rock gave analysis I; angle of optical extinction, $\epsilon:c=47^\circ$; sp. gr. = 3.232; it encloses some magnetite. The felspar (labradorite) gave II; after deducting magnesium and iron (due to enclosures of magnetite and augite) this gives Ab_3An_9 ; the angle of optical extinction on (010) is 22° ; sp. gr. = 2.697. The bulk analysis of the fresh rock is given under III; sp. gr. = 3.026. The partially weathered rock gave IV; here, as shown by microscopical examination, the olivine has been altered. As shown by this analysis, practically the only change is a slight hydration, and loss of magnesia. The completely weathered product gave V.

	SiO ₂ .	Al ₂ O ₃ .	Iron as Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	48.83	4.41	10.01	20.51	17.11	—	—	—	100.87
II.	49.65	24.49	5.98	11.02	4.31	[4.55]	—	—	100.00
III.	45.73	13.48	11.60	9.92	15.40	3.24	0.47	0.94	100.78
IV.	47.87	14.43	11.55	10.45	10.58	3.47	0.61	1.82	100.78
V.	37.09	13.19	35.69	0.41	0.57	1.75	0.33	11.83	100.86
IIIa.	12.78	9.10	8.75	4.37	8.65	not det.		0.94	44.59
IVa.	not det.	10.93	5.83	4.49	4.28	0.91	0.45	1.82	28.71
VA.	12.72	8.22	28.25	0.02	0.20	1.00	0.20	11.83	62.44

Calculating from III and V, on the assumption that the ferric oxide has remained constant in amount, it is seen that there has been a total loss of 70.31 per cent. of the original material, and that 73.64 per cent. of the original silica, 68.19 of the alumina, and most of the lime, magnesia, and alkalis have been removed.

The analyses of the portions of the fresh rock, partially altered rock, and completely decomposed material, which are soluble in half-normal hydrochloric acid and in sodium carbonate solution, are given under IIIa, IVa, and Va respectively. The three samples of material were digested with hydrochloric acid of different strengths, and the several analyses of the soluble portions show slightly varying results. Experiments show that the acid acts on the various minerals in the same order as do the processes of weathering, the olivine being attacked first, and the augite and magnetite last.

L. J. S.

Meteorite from Toubil, Gov. Yeniseisk. By A. KHLAPONIN (*Verh. russ.-kais. min. Ges.*, 1898, **35**, 233—241).—This meteorite was found in 1891, in the placers of the stream Toubil, dist. Atchinsk, gov. Yeniseisk, Siberia, and about 265 miles from Krasnoïarsk; it weighs 21,962 grams, and measures $23 \times 17.8 \times 11$ cm. Etched surfaces show well-marked, triangular Widmanstätten figures. The hydrochloric acid residue consists of black, carbonaceous matter, gelatinous silica, and needles of rhabdite. Analysis of the last (on 17 mg.) gave,

Fe.	Ni (and trace Co).	P.	Total.
53.53	34.12	9.41	97.06.

This gives the formula $\text{Fe}_3\text{Ni}_2\text{P}$, whilst the usual formula for rhodite is $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$. The bulk analysis of the meteorite is,

Fe.	Ni.	Co.	Ca.	Mg.	SiO_2 .	Mn.	As.
95.183	3.385	0.140	0.205	0.033	0.075	0.090	0.019
Cl.	C.	O.	S.	Rhadtite.	Total.		
0.038	0.120	0.093	Nil	0.425	99.806.		

Assuming the silica, magnesium, and calcium to be present as monticellite, there is still an excess of calcium to be accounted for. The oxygen shown above probably represents rust. L. J. S.

Jerome (Kansas) Meteorite. By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1898, [iv], 5, 447—454).—This stone was found in 1894 on the Smoky Hill River, about 15 miles east of Jerome, in Gove Co., Kansas. The largest piece weighs 62 lbs., and measures $12 \times 9 \times 10$ in., the smaller pieces weigh altogether $3\frac{1}{4}$ lbs. The surface is covered with a thin, dark-brown crust, and is somewhat weathered. The structure is fine-grained and compact. Sp. gr. = 3.466. Under the microscope are seen numerous chondrules of bronzite and of olivine, with fragmentary crystals of olivine, bronzite, and a little pyroxene, in a rather brecciated ground-mass of the same minerals, together with some interstitial matter, which seems to be glass; there are a few fragments of plagioclase, but no troilite was seen. Nickel-iron is present as small, angular masses partly altered to limonite. For the separation of the metallic iron, Eggertz's iodine method was used, but a good method is wanted for the determination of iron, ferrous oxide, and ferric oxide, and of nickel and nickelous oxide, &c.; some suggestions are given in the paper. Analysis of the nickel-iron gave,

Fe.	Ni.	Co.	Cu.	Total.
89.69	10.01	0.32	not det.	100.00

From the analyses of the portions soluble and insoluble in hydrochloric acid, the bulk analysis and the following mineralogical composition of the stone are calculated. Nickel-iron, 4.3; troilite, 5.2; chromite, 0.9; schreibersite?, 0.8; olivine, 30.2; bronzite, 23.6; pyroxene, 5.0; oligoclase, 6.6; orthoclase, 1.6; limonite, 20.2; NiO , 1.6 = 100.0. L. J. S.

San Angelo Meteorite. By H. L. PRESTON (*Amer. J. Sci.*, 1898, [iv], 5, 269—272).—This iron was found in 1897 partially buried in the soil on the prairie called "Lipan Flats," seven miles south of San Angelo, in Tom Green Co., Texas. It weighs 88 kilos, and measures $51 \times 29 \times 14$ cm.; the surface shows large pittings and is much oxidised, whilst a broken surface shows a well-marked octahedral structure. On an etched surface, rhombic-shaped Widmanstätten figures are sharp and distinct, and the so-called Laphamite lines are prominent. Troilite nodules are scarce. Small fissures, rarely filled with a substance resembling graphite, sometimes follow the lines of the Widmanstätten figures (compare this vol., ii, 343). Sp. gr. 7.7; analysis by Mariner and Hoskins gave,

Fe.	Ni.	Co.	Cu.	P.	S.	Mn.	Si.	C.	Total.
91.958	7.860	trace	0.040	0.099	0.032	trace	0.011	trace	100.000.

L. J. S.

Mineral Water of the Royal Springs of S. Agnese at the Bagno of Romagna. By ATTILIO PURGOTTI and G. ANELLI. (*Gazzetta*, 1898, 28, i, 349—355).—The mineral water of the Royal Springs of S. Agnese at the Bagno di Romagna issues at 40—43·7° and is credited with therapeutic properties; it has the sp. gr. 1·00088 at 15°/4°, and 10,000 grams contain the following dissolved constituents in grams.

CaH ₂ (CO ₃) ₂	0·1735	NaI	0·00019
NaHCO ₃	11·0074	Na ₂ B ₄ O ₇	1·1484
K ₂ SO ₄	0·1325	SiO ₂	0·3060
Na ₂ SO ₄	0·1049	CO ₂ (free).....	0·2200
MgCl ₂	0·1187	Organic matter...	0·0110
LiCl	0·0034	O ₂ at N.T.P.....	10 c.c.
NH ₄ Cl	0·0585	N ₂ „	54 c.c.
NaCl	0·2116	CH ₄ „	108 c.c.
NaBr	0·00093		

W. J. P.

Water of the Sacred Well at Mecca. By MAURITS GRESHOFF (*Rec. Trav. Chim.*, 1897, 16, 354—355).—The following table gives the results of analyses (expressed in grams per litre) made by Van Romburg in 1886, I. and by the author in 1896, II.

Residue at		Cl.	SO ₃ .	N ₂ O ₅ .	CO ₂ .	SiO ₂ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	P ₂ O ₅ .	
I.	180°.	3·165	0·556	0·395	0·725	0·317	0·047	0·412	0·152	0·578	0·272	traces.
II.		3·592	0·663	0·412	0·464	0·486	0·052	0·515	0·157	0·916	0·224	traces.
Sp. gr.		I=1·0025 at 18°.					II=1·0026 at 15°.					

J. J. S.

Physiological Chemistry.

Comparative Physiology of Digestion. I. Digestion of the Larva of *Tenebrio Molitor* (Meal-Worm). By WILHELM BIEDERMANN (*Pflüger's Archiv.*, 1898, 72, 105—162).—The paper is mainly anatomical and histological. The most important chemical points noted are, (1) the presence in the epithelial cells of the mid-gut of a number of crystalline clumps, which are of proteid nature, and which function as 'reserve material.' (2) The existence of an acid reaction in the upper half of the mid-gut; this is independent of the food taken, and is also found in the fasting condition. The contents of the lower part of the intestine are alkaline; this corresponds with anatomical differences in the cells of the lining epithelium. The acidity is due to acid phosphates. (3) The juice contains an energetic amylolytic enzyme, converting starch into dextrose, and an inverting enzyme, but no cellulose dissolving enzyme (cytase) was discovered. The course of proteolytic digestion closely resembles that by trypsin; tyrosine, but not leucine, crystals were separated out from the final products. Fats are split into fatty acids and glycerol; fat is not absorbed in the form of an emulsion.

W. D. H.

Gastric Digestion of Caseinogen. By FRANZ ALEXANDER (*Zeit. physiol. Chem.*, 1898, 25, 411—429).—The products of peptic digestion were separated by Pick's method of fractional precipitation with ammonium sulphate. The results, on the whole, closely coincide with those he obtained with Witte's peptone. The peptones obtained do not give Millon's reaction. Some of the results appear to indicate that mixed with caseinogen is a small amount of an albuminate.

W. D. H.

Digestion of Caseinogen by Pancreatic Juice. By UGO BIFFI (*Virchow's Archiv.*, 1898, 152, 130—157).—Under favourable circumstances, caseinogen is completely digested, about 4 per cent. of the weight of the proteid being removed as tyrosine. Casein-antipeptone has the percentage composition: C, 49.7; H, 7.2; N, 16.3; O, 25.2; S, 1.3; otherwise, it shows the properties and reactions of fibrin-antipeptone; the proteoses also agree in their reactions with those obtained from fibrin. The phosphorus of the caseinogen is found in two forms in the products of digestion, namely, as phosphoric acid, and as a compound not precipitable by magnesia mixture. The amount of phosphoric acid increases with the duration of the digestion and the amount of ferment present.

W. D. H.

Behaviour of Proteids which contain Phosphorus, in Metabolism. By FRANZ STEINITZ (*Pflüger's Archiv.*, 1898, 72, 75—104).—The present experiments, made on dogs, were carried out in the usual way by analyses and comparison of the intake and output in urine and faeces; the special point investigated, however, was whether proteids containing phosphorus lead to the laying down of phosphorus in the body. The proteids used were casein and vitellin; in the case of vitellin, however, there was some doubt as to whether it was not mixed with lecithin. The phosphates passed in the urine are, of course, allowed for. The general result of the experiments is that a considerable proportion of the phosphorus is retained in the body; the similar experiments previously made by Marcuse on casein led to the same result, but the proportion he found retained within the body was smaller. Relatively more nitrogen than phosphorus (compared to what is present in the casein given) is retained; this proportion between nitrogen and phosphorus retained was smaller in the experiments in which vitellin was used, but greater than in those where nucleo-histon was employed.

Control experiments were made with myosin, which was obtained almost free from phosphorus. Feeding with proteids containing phosphorus appears to yield better results so far as the putting on of phosphorus is concerned, than feeding with phosphorus-free proteids plus inorganic phosphates.

W. D. H.

Metabolism during Thymus-feeding. By THEODOR COHN (*Zeit. physiol. Chem.*, 1898, 25, 507—510).—In the urine of dogs fed on calf's thymus, a crystalline sediment is found, which, on examination, proved to be allantoin. This substance is believed to be the end-link

in the series of products from nuclein; possibly it arises from the oxidation of uric acid. In man, no such sediment was found.

W. D. H.

Physiological Relationships of Ammonia, and the Rôle of the Liver in Metabolism. By SERGEI SALASKIN (*Zeit. physiol. Chem.*, 1898, 25, 449—491).—Arterial blood shows great constancy in the amount of ammonia in it. The blood of the portal vein contains large quantities during digestion (3.5 to 8.4 milligrams per 100 grams of blood); the blood of the hepatic vein contains about the same amount as arterial blood. The alimentary mucous membrane is richer in ammonia after a meal of meat than after one of bread and milk. The lymph during digestion contains less ammonia than arterial blood, whilst the other organs exhibit great variations in the amount they contain. Such observations lend support to the views of those physiologists who believe in ammonia as a precursor of urea. In dogs with an Eck-Pawlow fistula, the ammonia in the blood, brain, and other organs goes up; the amount of urea falls, whilst that of ammonia increases in the urine. Ammonium carbamate is believed to be an important step in urea formation, but whether oxidising ferments play any important part in urea formation is left an open question; it, however, appears evident that the liver is not the sole seat of the process. Some observations on pathological cases in man are recorded which bear out the conclusions arrived at by experiments on animals.

W. D. H.

Changes in the Blood after Removal of the Thyroid. By A. G. LEVY (*J. Pathol. and Bacteriol.*, 1898, 5, 316—330).—The experiments were made on dogs.

There is reduction in the number of red corpuscles and of hæmoglobin, but this is not very intense or constant; the white corpuscles, on the other hand, are increased, but the numbers from day to day fluctuate considerably. The specific gravity of the blood always diminishes, and the percentage of fibrin is invariably increased. The total solids are lessened, and there appears to be an increase in some non-proteid constituent; the proteids and total nitrogen are diminished.

W. D. H.

Absorption of Iron in Man. By G. HONIGMANN (*Virchow's Archiv.*, 1898, 152, 191—192).—Hoffmann's experiments on animals prove that absorption of inorganic preparations of iron takes place in the intestine. The present observations on a patient with a fistula in the lower ileum, and in whom the large intestine was thus rendered functionless, show, from examination of the intestinal contents during the administration of *ferrum citricum oxidatum*, that Bunge's hypothesis has no foundation, and that the alimentary canal, as far as the ileum has the power to absorb as much, is 0.33 gram of iron in two days. The urine only contained traces of iron.

W. D. H.

Iron in the Liver and Spleen. By J. EVERETT DUTTON (*J. Pathol. and Bacteriol.*, 1898, 5, 331—339).—Histo-chemical and macro-chemical examination of museum specimens of liver and spleen from two cases of malaria shows that there is an enormous increase of the

iron in these organs in that disease, produced by blood destruction. The following are the figures obtained compared with those obtained by Quincke in normal cases.

		Milligrams of iron per 100 grams of organs.	
		Liver.	Spleen.
Healthy case,	1	30—40	253
„	2	81	144
Malarial	1	208	1135
„	2	440	1325

W. D. H.

Phenylic Phosphates in the Animal Body. By WILHELM AUTENRIETH and ZOLTÁN VON VAMÓSSY (*Zeit. physiol. Chem.*, 1898, 25, 440—448).—It is shown that the normal phenylic and chlorophenylic phosphates are so decomposed in the animal body that a decomposition product, a diphenylphosphoric acid of the common formula $OP(OR)_2OH$, is formed.

W. D. H.

The Urea-forming Ferment of the Liver. By OTTO LOEWI (*Zeit. physiol. Chem.*, 1898, 25, 511—522).—Richet and others have stated that the ‘surviving’ liver and extracts of the organ are capable of transforming amido-acids into urea. It is difficult to consider that such an action, if it does occur, is a ferment action in the usual sense of that term. Attempts to repeat the experiments with glycocine failed, no urea being formed; there is, however, a formation of a nitrogenous substance, the nature of which is uncertain, but which resembles urea in some of its characters.

W. D. H.

Formation of Animal Fat. By W. LUMMERT (*Pflüger's Archiv.*, 1898, 71, 176—208).—From the researches of others, it appears probable that animals are not capable of building up fatty tissue from proteids; the following experiments were made to determine the quantity and nature of the fat elaborated by animals from carbohydrates when fed solely on the latter and proteid matter deprived of fat. Each animal was starved until it had lost considerably in weight, in order to deprive the fat-cells of their contents, and was then fed on flesh, rice-starch, casein, and meat-extract. It was found that, although ducks and geese increased considerably in weight on this diet, hardly any adipose tissue was formed; dogs, on the other hand, produced large quantities of fat, which, when examined according to the directions given in Benedikt's “Analyse der Fette und Wacharten,” 3rd edition, 1897, gave values showing that the fats formed consist of the triglycerides of palmitic, stearic, and oleic acids, mixed in similar proportions to those characterising other natural fats. Of special interest is the fact that in the fats elaborated from carbohydrates, neither hydroxy-fatty acids nor alcohols of the fatty series are present.

In the liver, no fat formation appears to take place under the conditions of diet described; the amount of fat corresponded with that present in dogs after long periods of starvation. The substances extracted by light petroleum from the dried liver of the dogs were found to constitute from 4.9—8.7 per cent. of its weight, and to contain from 23.3—34.9 per cent. of cholesterol; the fat formed in the

region of the spleen and the kidneys also contains from 13—22 per cent. of cholesterol.

The blood yielded from 0.9—1.15 per cent. of its weight of solid substances soluble in light petroleum, and judging from the acetyl-number, these apparently contain from 54.9—61.3 per cent. of cholesterol; it would appear that their amount is increased by a change from a proteid to a mixed proteid and carbohydrate diet, fat being excluded.

W. A. D.

Formation of Uric Acid. By J. WEISS (*Zeit. physiol. Chem.*, 1898, 25, 393—397).—On the addition of certain fruits (cherries, grapes, &c.) to the author's diet, the amount of uric acid in the urine diminishes, whilst that of hippuric acid (which normally is only present in traces) increases. Experiments were then made with the individual constituents of fruits, namely, potassium hydrogen tartrate, tannic acid, sugar, and quinic acid, but the last named substance was the only one which produced the rise of hippuric and fall of uric acid. Glycerol and lactic acid gave a negative result; the urine throughout was acid.

W. D. H.

Oxidation of the Stereoisomeric Tartaric Acids in the Animal Organism. By ALBERT BRION (*Zeit. physiol. Chem.*, 1898, 25, 283—295).—Pohl (*Arch. exp. Path. Pharm.*, 37, 411) has shown that tartaric acid is only partially oxidised in the organism of a dog or rabbit, whereas substances such as erythritol, succinic acid, and malic acid, which might be expected to give tartaric acid under the above conditions, are completely decomposed.

The author has made a number of experiments on the oxidation of the isomeric tartaric acids in the organism of a dog, and finds that *l*-tartaric and mesotartaric acids are most completely oxidised, *d*-tartaric acid much less, and least of all racemic acid. It follows, therefore, that racemic acid is not split up into its components during its passage through the animal organism.

A. W. C.

Oxidation Changes produced by Animal Tissues. By WILHELM SPITZER (*Pflüger's Archiv.*, 1898, 71, 596—603).—In continuation of previous work, in which it has been shown that the oxidation changes produced by animal tissues and tissue extracts depend on the presence of nucleo-proteids (this vol., ii, 36), it is now shown that this is also true for the conversion of arsenious into arsenic acid.

Hofmeister having advanced the opinion that urea can be formed by oxidation processes, the experiment of attempting to obtain urea by digestion of liver-extracts with various ammonium salts was made, but with negative results.

W. D. H.

Composition of Fish, Crustacea, and Molluscs. By BALLAND (*Compt. rend.*, 1898, 126, 1728—1731).—The author has determined the moisture, nitrogen, fat, ash, and extractives in the uncooked flesh of 38 kinds of fish, &c.; the results may be compared with those obtained by Miss Williams (*Trans.*, 1897, 649) in the analysis of cooked fish. It appears that those fish which contain the least amount of water are the richest in fat, whilst those containing the least fat are

the richest in nitrogen. Crustacea and molluscs contain, as a rule, both less nitrogen and less fat than fish. N. I.

Composition of Colostrum. By HUGO TIEMANN (*Zeit. physiol. Chem.*, 1898, 25, 363—392).—The colostrum of different cows differs in composition; the specific gravity varies from 1·0299 to 1·0594, and diminishes with each milking; the amount of dry residue varies from 12·83 to 32·93 per cent., but the greatest variation is in the amount of fat present. The nitrogenous constituents diminish, but the sugar increases, with successive milkings. The amount of true albumin is small; the amount of caseinogen is about the same as in normal milk, or higher. The amount of globulin (probably combined with calcium) is from two to four times as much as that of caseinogen; this globulin is not in solution but in suspension, and it coagulates at 72°. It has the percentage composition, C, 49·83; H, 7·77; N, 15·28; S, 1·24; O, 25·88. Serum-globulin contains C, 52·71; H, 7·01; N, 15·85; S, 1·11; O, 23·32. W. D. H.

Abnormal Milk. By R. GREIG SMITH (*J. Soc. Chem. Ind.*, 1894, 13, 613—614).—Analyses are given of milk from two different cows, the cream of which could be converted into butter by simply stirring with a stick, without the use of a churn. In both samples, the quantity of fat was slightly less than that calculated by Droop Richmond's formula, although the butter produced had a normal composition. In the ash, there appeared to be a deficiency of potassium and an excess of calcium salts. The fat globules of both samples had an average diameter nearly double that of the globules of milk obtained from the Jersey cow, the maximum diameter being as great as 0·001 inch. The abnormal properties of the milk are probably to be attributed to the size of the fat globules. W. A. D.

Examination of Sheep's Milk, with Special Regard to the East Friesland Breed. By HERMANN HUCHO (*Bied. Centr.*, 1898, 27, 391—392; from *Landw. Jahrb.*, 1897, 26, 497).—Three East Friesland sheep, five, one, and two years old, gave about 205, 105, and 198 kilos. of milk in a year. The average percentage composition of the milk of the three sheep was as follows.

	Sp. gr.	Dry matter.	Fat.	Proteids.	Milk-sugar.	Ash.
I	1·0357	17·47	6·90	5·41	4·35	0·81
II	1·0379	16·79	6·09	5·44	4·47	0·97
III	1·0374	16·45	5·70	5·33	4·55	0·87
I—III { Lowest	1·0319	14·18	4·15	3·90	3·12	0·71
{ Highest	1·0440	23·45	10·80	8·93	5·42	1·12

The fat and proteids are thus higher, the milk-sugar lower, than is the case with cows' milk. The colostrum was rich in fat (7—9 per cent.) and proteids. Although the three sheep were selected as patterns, the yield of milk was much less than the amounts often stated to be obtained. After lambing, the sheep only weighed 51·5—56 kilograms, and gave only 3·15—3·45 kilograms of wool, which, however, was not of bad quality.

Merino, Hampshire, and two other varieties of sheep, the milk of

which was examined, on a few days gave 40—80 kilos. of milk, reckoned on the whole period of lactation, containing 3.0—4.5 per cent. of fat.

N. H. J. M.

Uric Acid Crystals. By SCHREIBER (*Virchow's Archiv.*, 1898, 153, 147—151).—Ebstein stated that, after treating crystals of uric acid, or urinary gravel, with dilute alkali, the pigment is removed, and the remaining crystals retain their original form and power of double refraction. They give no proteid reaction. Moritz and Mendelssohn, on the other hand, allege that the crystals have a stroma or substratum of proteid nature.

The present research to reinvestigate the question, undertaken under Ebstein's directions, confirms Moritz's statement that, after dissolving out the uric acid with a solution of lysidine and tannic acid, a 'shadow' of the crystal remains behind, which is optically inactive. The same is true for uric acid crystals artificially crystallised from an albuminous liquid. After the uric acid is purified by repeated recrystallisations, this does not occur. The so-called 'shadow,' however, gave none of the proteid reactions.

W. D. H.

Physiological Action of Butyric and β -Hydroxybutyric Acids. By WILHELM STERNBERG (*Virchow's Archiv.*, 1898, 152, 207—217).—Butyric acid injected intravenously in animals (cats) produces coma, but synthetically prepared β -hydroxybutyric acid does not produce this effect. This acid is optically inactive; that found in diabetics is the optically active acid. This consideration, however, is believed not to militate against the conclusion drawn, namely, that diabetic coma is not due, as Minkowski considers, to β -hydroxybutyric acid; the cause of the coma is stated to be a lessening of the alkalinity of the blood.

W. D. H.

The Poisonous Action of Urine. By ADOLF BECK (*Pflüger's Archiv.*, 1898, 71, 560—595).—The convulsions which follow the injection of urine into the circulation are not due to its action on the cerebral cortex, for they arise also in animals in which the hemispheres have been removed. They are probably a symptom of dyspnoea, which is produced by disordered circulation in the bulb.

The principal action of urine is on the heart, which is paralysed; the effect on the respiration is secondary to this.

The toxic agents in the urine are its potassium salts, not ptomaines, as Bouchard thought. The antagonism between the urine of the day and night on which Bouchard lays so much stress in his theory on sleep does not exist. The toxic action of both varieties of urine is the same.

W. D. H.

The Experimental Production of "Amyloid" Disease. By N. KRAWKOFF (*Virchow's Archiv.*, 1898, 152, 397—398).—The failure of Lubarsch to produce amyloid degeneration artificially in animals is attributed to certain faults in the method he adopted.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Progress of Fermentation Chemistry during the Last Decades. By MAX DELBRÜCK (*Ber.*, 1898, 31, 1913—1925).—An historical lecture, tracing the course which has been followed by the chemistry of fermentation during recent years. M. O. F.

Alcoholic Fermentation without Yeast Cells. By HANS ABELES (*Ber.*, 1898, 31, 2261—2267. Compare this vol., ii, 127, 246, 346, and 396).—The author discusses the results of Buchner's experiments on the action of antiseptics, and strong solutions of sugar and glycerol on yeast extract, and the apparent differences noticed in the case of living yeast cells.

The amount of extract obtained from yeast, and the microscopic examination of the press cakes, indicate that not only the liquid portion, but also the protoplasmic contents of the cell are present in the expressed juice. The author accordingly compares the results of experiments on living yeast cells with those on yeast extract containing the same percentage amount of cell-contents, and finds that the inhibiting action of sodium arsenite, chloroform, toluene, and ammonium fluoride is quite similar in both cases. Experiments made with strong solutions of cane-sugar and glycerol also indicate that, in mixtures containing the same percentage amount of cell-contents, the effect of these agents on the activity of yeast extract is the same as that on emulsions of living yeast cells. The author, after discussing other arguments which are supposed to tell against the existence of living protoplasm in the extract, concludes that there is but little difference between the fermenting agents in the living cell and in the extract, and that the activity of the latter is best explained by assuming that it still contains living protoplasm. G. T. M.

Production of Acid by Bacteria in Nutritive Media. By WILLIAM HANNA (*J. Pathol. and Bacteriol.*, 1898, 5, 267—273).—The production of acid is used to distinguish between *Bacterium coli* and *B. typhosus*. In milk, the acid doubtless originates from lactose; both the bacteria named above, however, produce acid. Acid production and curdling of the milk are not necessarily concomitants. In diluted serum to which carbohydrate is added, acid production may also occur. The amount of acidity may be determined by titration, and observations on a large number of micro-organisms are recorded. Of the carbohydrates used, lactose and dextrose appear to be most readily acted on, with the formation of acid. W. D. H.

Microbiology of the Process of Nitrification. By SERGEI WINOGRADSKY (*Centr. Bakt. Par.*, 1896, 2, ii, 415—428, and 449—458).—Burri and Stutzer isolated a nitrate organism which showed relatively luxuriant growth on broth and gelatin, but at the same time lost its nitrifying power. The author's experiments, made with a pure cultivation obtained from Burri and Stutzer, showed that, besides the

nitrate organism, another, morphologically very similar, organism was present, which develops in organic solutions. The following conclusions are drawn.

The oxidation of nitrites to nitrates must at present be considered as a strictly specific function, incompatible with the property of decomposing organic, especially highly nitrogenous, matter. This function is not labile, but is inseparable from the vitality of the microbe, the development of which is only possible in conjunction with the oxidation of nitrites. The divergent results of Burri and Stutzer arose from an experimental error, and a nitrate bacillus which thrives on gelatin is at present unknown.

N. H. J. M.

Denitrification. By G. AMPOLA and C. ULPIANI (*Gazzetta*, 1898, 28, i, 410—438).—The authors have succeeded in isolating two new denitrifying organisms; one, *Bact. denitrificans V*, is obtained from earth, and the other, *B. denitrificans VI*, infects suitable media on exposure to the air.

From the results obtained on cultivating these organisms and examining the products of their action on the medium, the authors conclude that the process of denitrification can be expressed by the equation, $5\text{C}_6\text{H}_{12}\text{O}_6 + 24\text{KNO}_3 = 24\text{KHCO}_3 + 6\text{CO}_2 + 18\text{H}_2\text{O} + 12\text{N}_2$.

W. J. P.

The Nitrate Fungus. By ALBERT STUTZER and R. HARTLEB (*Chem. Centr.*, 1897, ii, 622—623; from *Centr. Bakt. Par.*, 3, ii, 351—354).—About 89—93 per cent. of nitrogen as nitrites is converted into nitrate by the nitrate-bacteria; carbonates, chlorides, and sulphates are favourable, but calcium chloride is unfavourable, to nitrification. Nitrates are not produced in presence of ammonium salts, but only after the whole of the ammonium salts within reach of the organisms have been converted into nitrites.

N. H. J. M.

The Principal Amide of the Sugar-cane. By EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1897, 19, 881—889).—It has long been known that in many plants a portion of the nitrogen present exists in the form of amides, the amount varying with the life and condition of the plant. Crystalline specimens of an amide, obtained from cane-juice by previous observers, have been assumed to be asparagine, but the author finds that the principal amide of the sugar-cane is optically inactive and is not asparagine, but glycocine; the latter compound has not hitherto been known to occur in plants. Fifteen preparations of glycocine, made from samples of the cane during various stages of growth, indicate that this amido-acid is a normal constituent throughout the life of the plant. Glycocine is most easily distinguished from asparagine by the reaction with hot solutions of alkalis. Even with dilute alkali, asparagine readily evolves ammonia with the production of aspartic acid; glycocine, however, gives no ammonia unless the solution is strongly alkaline, and after the evolution of ammonia has ceased only hydrocyanic and oxalic acids are found in solution.

Since the glycocine of sugar-cane has been mistaken for asparagine, it is possible that its presence may have been overlooked in other plants. Should it occur in the *Graminæ*, which form the major portion

of the food of herbivorous animals, this would help to account for the relatively large quantity of hippuric acid found in the urine of these animals.

Glycoccine is probably the form in which nitrogen is conveyed to the growing parts of the sugar-cane, and, as maturity is reached, it is converted into proteids, which again furnish glycoccine when a fresh growth takes place. There appears to be in the cane a gelatin, or gelatin-yielding proteid which gives glycoccine as a product of decomposition.

G. T. M.

The Sugar-cane Amide. By EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1898, 20, 133—137).—The amido-substance present in the juice of the sugar-cane is glycoccine, as with benzoic chloride it gives rise to hippuric acid, which was identified by its analysis, appearance, and solubility. The melting points of the amido-substance and the hippuric acid obtained from it are, however, not given.

W. A. D.

Lecithins of Sugar-cane. By EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1898, 20, 113—118).—On precipitating the proteids of raw cane-juice with cupric hydroxide and filtering, a solution is obtained which yields a chocolate coloured precipitate with sodium phosphotungstate dissolved in dilute sulphuric acid; on triturating the dried precipitate with powdered sodium carbonate, extracting with 95 per cent. alcohol, evaporating to dryness, dissolving in water, and extracting with ether, a wax-like substance is obtained, which appears to be a mixture of several lecithins. On digesting it with barium hydroxide, and decomposing the salts formed with sulphuric acid, oleic acid is obtained, together with palmitic and stearic acids; betaine and choline were also isolated, but it is not yet certain whether they existed free in the original juice, or were wholly produced by the hydrolysis of the lecithins. It appears that phosphotungstic acid precipitates from cane-juice, together with the lecithins, a colouring matter, which contains no nitrogen, and is probably a glucoside.

From the above work, it follows that the method generally adopted of designating as "amide-nitrogen" the difference between the total nitrogen of the juice and the "albuminoid" nitrogen present in the cupric hydroxide precipitate is one liable to considerable error; a large proportion of the so-called amide-nitrogen is attributable to substances present of the type of the lecithins.

W. A. D.

Lecithin in Plants. By JULIUS STOKLASA (*Zeit. physiol. Chem.*, 1898, 25, 398—405).—From analyses of lupins at flowering time, the conclusion is drawn that the formation of lecithin and proteids depends on photosynthetic assimilation, the chloroplasts working with the energy derived from the sun's rays. The chlorophyll-free cells of fungi form their proteid and lecithin molecules by other processes, concerning which a later communication is promised.

W. D. H.

Proteids of Lupin Seeds. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1897, 19, 454—482).—Both yellow lupin (*Lupinus luteus*) and blue lupin (*L. angustifolius*) seeds contain very little proteid matter soluble in water. In the case of yellow lupin, the amount is only some 0.37 per cent.; a part of this consists

of proteose, and the remainder is either albumin or a globulin readily soluble in very dilute saline solutions. Peptone is not contained in the freshly ground seed, but is formed in small quantity after prolonged contact with water. Yellow lupin seeds yield as much as 26.2 per cent. of proteid matter soluble in saline solutions; this is Ritthausen's conglutin. Preparations from blue lupin are usually much purer than those from the yellow, for the latter contain a considerable amount of some substance containing sulphur, from which conglutin can be separated by fractional precipitation out of dilute salt solutions. This explains why Ritthausen's conglutin from the yellow lupin contained twice as much sulphur as that from the blue lupin. When purified, no difference in properties and reactions can be detected between preparations from the two seeds. The results of a number of analyses gives the following percentage composition. Conglutin from yellow lupin, C=50.91; H=6.88; N=17.93; S=0.52; O=23.76. Conglutin from blue lupin, C=51.13; H=6.86; N=18.11; S=0.32; O=23.58. Conglutin is readily soluble in sodium chloride solutions containing upwards of 5 per cent. of the salt; on sufficient dilution, it is precipitated, a syrupy liquid separating which is rendered opaque and solid by treatment with water. When dissolved in salt solution, it appears not to be affected by prolonged heating in a boiling water bath, but solutions thus heated, when allowed to cool, form a solid, opalescent jelly, which becomes clear and fluid on further heating. Unlike other globulins, conglutin does not yield insoluble (coagulated) products when washed with alcohol, or when dried.

The lupin meal, which has been extracted with salt solution, yields a small quantity of proteid when exhausted with 0.2 per cent. potassium hydroxide solution. This proteid can be precipitated by adding acetic acid in slight excess, but not by making the solution neutral to litmus. Its percentage composition is, carbon=51.40; hydrogen=6.79; nitrogen=16.43; sulphur=1.03; and oxygen=24.35 per cent.

J. J. S.

Proteids of the White Poddad Adzuki Bean (*Phaseolus radiatus*). By THOMAS BURR OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1897, 19, 509—513).—*Phaseolus radiatus* is a small, red bean, cultivated in Japan; its chief globulin is phaseolin, identical with that obtained from the white bean (Abstr., 1896, i, 454). A small quantity of another globulin is also present; this can only be partly removed from its solutions by dialysis into water, but is wholly separated, in a coagulated form, by dialysis into alcohol. The same globulin has also been found in the pea, vetch, and cow pea. Its composition is, carbon=53.97; hydrogen=7.01; nitrogen=16.31; sulphur=0.88; and oxygen=21.83 per cent.

J. J. S.

Proteids of the Pea. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, 20, 348—362. Compare Abstr., 1896, i, 715).—It has been found that the legumin of the pea is always contaminated with more or less vicilin, a proteid first obtained from the horse-bean, *Vicia faba*. When the vicilin is completely removed, the differences previously noted between the legumin of the

pea and that of the vetch disappear, and preparations from these two seeds are identical in composition and reactions. Legumin is not coagulated when its solutions are heated; vicilin, on the other hand, becomes coagulated when its solutions are heated to 95—100°; it is also soluble in a more dilute brine than legumin. Besides these two globulins, two other proteids are present in the pea, namely, *proto-proteose*, which is precipitated by the addition of acetic acid to a solution saturated with salt, and *deutero-proteose*, which is not precipitated by acetic acid.

The combined amount of legumin and vicilin obtained by dialysing extracts of the pea is about 10 per cent. J. J. S.

Proteids of the Lentil. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, 20, 362—375).—Coarsely ground lentils which had been freed from the outer seed coats by a current of air, were ground to fine flour, and the proteids extracted by a 10 per cent. solution of sodium chloride; the clarified and filtered extract being then subjected to fractional dialysis, and precipitation with ammonium sulphate. The products thus obtained were then subjected to careful fractional precipitation from dilute saline solutions, and by this means the same proteids as had been found in the pea (Abstr., 1896, i, 715, and preceding abstract) were obtained, namely, legumin, vicilin, legumelin, and proteose. The amount of the globulins extracted by water is much greater in the case of the lentil than in that of the pea, especially if the acid of the seed is first neutralised by barium hydroxide. J. J. S.

Proteids of the Horse-bean (*Vicia faba*). By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, 20, 393—405. Compare Ritthausen, Abstr., 1883, 675; 1884, 1405).—In order to avoid contaminating the proteids with tannin, which Ritthausen found to be present in considerable quantity in the skin of the beans, the greater part of the outer coating was removed from the coarsely broken seeds by a current of air, and the remainder by hand picking. The subsequent treatment was the same as in the case of the lentil (preceding abstract). The proteids isolated were the same as in the case of the pea and lentil, namely, legumin, vicilin, legumelin, and proteose.

The amount of these proteids extracted from the seed by water is about 16—18 per cent., the yield being slightly higher when the acid contained in the seed was neutralised with barium hydroxide before extraction; the unneutralised extract, unlike the neutralised, and unlike other extracts of legumes, gave a heavy precipitate with pure sodium chloride. The addition of acetic acid gave a large precipitate soluble in dilute brine; so also did calcium chloride and calcium sulphate.

J. J. S.

Proteids of the Vetch. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, 20, 406—410. Compare Abstr., 1896, i, 715).—The globulin, previously described, has been further fractionated, and the results indicate that the saline extracts of the

vetch contain no other proteids than legumin, legumelin, and a very small proportion of proteose. Vicilin, which occurs in the pea, horse-bean, and lentil, is not present in detectable quantity in the vetch.

J. J. S.

Proteids of the Pea, Lentil, Horse-bean, and Vetch. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, 20, 410—419. Compare Abstr., 1896, i, 715, and preceding abstracts).—The seeds of the pea, lentil, horse-bean, and vetch contain legumin, legumelin, and proteose; the pea, lentil, and horse-bean also contain vicilin. Full analytical numbers and descriptions of the properties and reactions of these proteids are given. The authors think that legumelin is to be classed with the albumins rather than with the globulins; the amount of legumelin present in the pea is 2 per cent., in the vetch 1·5, and in the lentil and horse-bean 1·25 per cent.

J. J. S.

Proteids of the Soy-bean—Glycine Hispida. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, 20, 419—428).—Two varieties of soy-bean have been examined, namely, yellow soy-bean and the variety known in Japan as *Kiyusuki diadzu*. The seeds were treated as in previous cases (preceding abstracts). The chief proteid is a globulin somewhat similar to legumin, but of different composition, containing nearly twice as much sulphur, 0·4 per cent. more carbon, and 0·5 per cent. less nitrogen. The authors term this proteid *glycinin*; its composition is: carbon = 52·12; hydrogen = 6·93; nitrogen = 17·53; sulphur = 0·79; and oxygen = 22·63 per cent. It is readily soluble in sodium chloride solutions, and is precipitated by dialysis, by dilution, or by cooling. Solutions containing more than 2 per cent. of sodium chloride dissolve glycinin freely, whilst the solvent power of those containing less salt diminishes more rapidly than the percentage of salt decreases. Dissolved in sodium chloride solution, the globulin is not precipitated by saturating with magnesium sulphate or sodium chloride, but is completely precipitated by saturating with sodium sulphate at 34°. When prepared from carefully neutralised extracts, glycinin is not soluble in pure water; if soy-bean meal is treated with water, upwards of 16 per cent. of the globulin is dissolved, but here the solution is due to the potassium phosphates contained in the seed. Its solution in 10 per cent. sodium chloride is not coagulated by prolonged heating in a boiling water bath. Dilute acetic acid yields a precipitate which is insoluble in excess of sodium chloride solution. The insoluble, so-called albuminate, form of this globulin, like that of legumin, when treated with salt solution, becomes gelatinous, and it is impossible to filter solutions containing even a small quantity of it. In absence of salts, glycinin is readily soluble in very dilute acetic acid, and is precipitated from such solution by sodium carbonate, even before the acid is completely neutralised.

The soy-bean contains a more soluble globulin, which is probably identical with phaseolin. It also contains about 1·5 per cent. of legumelin and a small quantity of proteose.

J. J. S.

Proteids of the Sunflower Seed. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1897, 19, 487—494. Compare Ritthausen, *Abstr.*, 1880, 677; Vines, *J. Physiol.*, 3, 93).—The meal of the seeds was freed from oil and then extracted with 10 per cent. sodium chloride solution; a quantity of proteid was obtained from this extract by dilution, by dialysis, and also by saturation with sodium chloride. In composition and reactions, this proteid agrees with the globulin edestin, except that a part of it is precipitated by saturating its solutions in brine with sodium chloride; in composition, the part precipitated by saturating with salt and that remaining in solution are alike. As obtained by extraction from the seed, it is probable that the globulin is mixed with some 2 or more per cent. of helianthotannic acid, from which it cannot be completely separated. The authors cannot confirm Vine's statement that, if the seeds are treated with alcohol instead of ether, the globulin contained in them becomes soluble in concentrated salt solution.

J. J. S.

Proteids of the Cow Pea (Vigna Catjang). By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1897, 19, 494—500).—The chief proteid of the cow pea is a globulin which the authors term *vignin*; it much resembles the legumin of the pea and vetch, but differs in composition and properties. Its composition is: carbon = 52·64, hydrogen = 6·95, nitrogen = 17·25, sulphur = 0·5, and oxygen = 22·66 per cent. It dissolves in cold or warm water free from dissolved salts, and may be precipitated from such solutions by the addition of a very little sodium chloride. It is readily soluble in saline solutions containing upwards of 5 per cent. of sodium chloride, but very little dissolves in a 1 per cent. solution. It is readily and completely soluble in dilute acids or alkalis in the absence of salts; but solutions in very dilute nitric or hydrochloric acid are precipitated by salt or by excess of these acids. It is much less readily soluble in dilute sulphuric acid, and is not precipitated by an excess of the acid. Dissolved in 0·5 per cent. sodium carbonate solution, the proteid is precipitated by neutralisation. When dissolved in 10 per cent. sodium chloride solution, it is precipitated on the addition of a considerable quantity of hydrochloric or acetic acid; the saline solution deposits the globulin on dilution more readily than do similar solutions of legumin; saturation with sodium chloride does not precipitate vignin, but saturation with sodium sulphate at 34° causes complete precipitation. Solutions in 10 per cent. brine become turbid when heated to 98°, and after continued heating set to a jelly.

In addition to vignin, the cow pea contains a small quantity of a globulin, probably phaseolin, and a third globulin can also be extracted; this is very readily soluble in very dilute salt solutions, and is partly precipitated by dialysis into water, and completely into alcohol. Its percentage composition is: carbon = 53·25, hydrogen = 7·07, nitrogen = 16·36, sulphur = 1·11, and oxygen = 22·21.

J. J. S.

Proteids of Bean Flour and Wheaten Flour. By ÉMILE FLEURENT (*Compt. rend.*, 1898, 126, 1374—1377).—A specimen of bean flour was found to contain 31·04 per cent. of nitrogenous con-

stituents, comprising legumin, 18.92 per cent. ; vegetable albumin, 0.20 per cent. ; glutenin, 9.52 per cent. ; and gliadin, 2.40 per cent. The value of wheaten flour is closely connected with the composition of the gluten, which should consist of glutenin and gliadin in the proportion of 1 to 3, and it is a common practice to improve certain varieties of wheaten flour by adding 2 or 3 per cent. of bean flour. The effect of this admixture is to maintain the proper ratio of glutenin to gliadin, bean flour being especially rich in glutenin, whilst wheaten flour is sometimes deficient in this substance.

N. L.

Decomposition of Proteids in Living Plants. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1897, 24, 18—114).—During germination, a mixture of nitrogenous compounds, in which aromatic and fatty amido-acids and arginine are probably invariably present, are produced in the decomposition of the proteids, and of the albumoses and peptones formed by the hydrolysis of the proteids. It may be questioned whether asparagine and glutamine are directly produced to any great extent, but this is by no means improbable. These products are to a great extent further decomposed, a portion of the nitrogenous residue (? ammonia) being utilised in the synthesis of asparagine and glutamine and possibly other compounds. The object of this process is to convert the products which are not suitable for producing proteids into material available for this purpose. Whether similar changes take place in plants subsequent to germination remains to be proved. At the same time, there is no evidence against such a supposition.

An examination of alcoholic extracts of etiolated lupin seedlings for amido-acids gave the following results. Seedlings of *Lupinus angustifolius* (6 days) yielded mainly leucine. Eight-day old seedlings furnished about 1 per cent. of amido-acids containing, besides leucine, a certain amount of tyrosine, and probably a little phenylalanine. Seedlings of *Lupinus luteus* (6 days) gave results similar, both qualitatively and quantitatively (as regards total yield), to 8-day old seedlings of *L. angustifolius*, but they probably contained arginine as well.

Estimation of Asparagine.—Finely ground seedlings, mixed with a little calcium carbonate, are extracted with hot water, and the filtrate evaporated to a thin syrup, being filtered a second time during the evaporation. The crystals of asparagine which separate after 1—2 days are washed with cold water and dilute alcohol, dried at 105° and weighed ; the mother liquor, &c., are evaporated to a syrup, and the crystals which separate placed on a porous plate, and afterwards crystallised from water. The whole of the crystals are weighed, the weight of the small amount of ash they contain being deducted.

N. H. J. M.

Solution of the Reserve Substances of Grain and Bulbs. By KONSTANTIN A. PURIEWITSCH (*Ann. Agron.*, 1898, 24, 288, from *Ber. deut. bot. Ges.*, 14).—When wheat and maize, from which the embryos and scutella have been removed, are kept in contact with distilled water (complete immersion being avoided), the reserve matter of the endosperm is dissolved out and the cells become empty as during germination. When saline or organic solutions are employed instead of

water, the emptying of the endosperm is greatly hindered, whilst it is completely stopped by treatment with ether or chloroform.

Lupins, haricots, and bulbs from which the embryos were removed gave similar results. The embryo is, therefore, not essential for the solution of the reserve substances, although it does undoubtedly secrete diastases, which penetrate to the albumen and accelerate its digestion.

Bulbs and cotyledons thus exhausted can be refilled by means of appropriate solutions. This was observed in the case of *Allium cepa*, which, after being kept 6 days in contact with a 5 per cent. solution of saccharose, was found to contain a considerable amount of glucose. With the endosperm of wheat and maize, however, negative results were obtained.

N. H. J. M.

Cascara Sagrada. By ALFRED R. L. DOHME and HERMANN ENGELHARDT (*J. Amer. Chem. Soc.*, 1898, 20, 534—546).—The air-dried powder of *Cascara sagrada* bark, after drying at 110° to constant weight, is shown to contain 8·3 per cent. of moisture. The ash (about 7 per cent.) contains sodium, potassium, aluminium with traces of calcium and iron, together with silicic acid and traces of hydrochloric and sulphuric acids.

On extracting with chloroform in a specially devised apparatus, it gives 7·5 per cent. of a dark greenish-brown oil, a portion of which is volatile with steam. It has a yellowish-green colour and to a marked degree the characteristic odour of the bark.

The residual oil contains neither alkaloid nor glucoside, but on saponification with potassium hydroxide yields a substance crystallising in white leaflets melting at 24—26° and having the composition $C_{12}H_{26}O$. It is probably normal dodecyclic alcohol, which melts at 24° and is present in combination with palmitic and stearic acids.

The residue from the chloroform extract, when treated with alcohol, gives a glucoside crystallising from acetone and ethylic acetate in dark brown-red needles melting at 237°. The authors propose to call this substance *purshianin*. On heating it with alcoholic hydrochloric acid, it yields a sugar and emodin.

A. W. C.

Investigation of Soil for the purpose of Judging its Mechanical and Chemical Properties. By KURT BIELER (*Jahrb. agrik.-chem. Versuchs. Stat.-Halle a.-S.*, 1896, 2, 146—155).—The soils examined were in part those of the experimental station itself, but mostly from elsewhere.

In estimating lime and phosphoric acid, for instance, in samples which have not been subjected to mechanical analysis, the air-dried soil (250 grams) is heated for half an hour on a water bath with 500 c.c. of water, being frequently stirred. The whole is then removed to a 0·2 mm. sieve and washed through with a brush; it is afterwards washed through gauze, and the dust thus obtained analysed. The results are calculated on the weight of air-dried fine sand, the weight of which, as well as of the dust, must be ascertained.

In judging the quality of a soil, the following numbers (per cent.), are used as a basis.

	N and P_2O_5 .	K_2O .	CaO in loam.	CaO in sand.
Poor... ..	below 0.05	below 0.05	below 0.10	0.05
Moderate... ..	0.05—0.10	0.05—0.15	0.10—0.25	0.10
Normal	0.10	0.15—0.25	0.25—0.50	0.1—0.2
Good	0.10—0.15		0.50—1.00	above 0.2
Rich.....	above 0.15	above 0.25	above 1.00	

As regards mechanical analysis, the amounts of soil are determined which are retained by 6, 3, 2, 1, 0.5, and 0.2 mm. sieve, the fine sand, and the dust. The dust is further separated by water into dust-sand and mud.

A large number of analyses are given in tables. N. H. J. M.

Reduction of Nitrates in Arable Soil. By PIERRE P. DEHÉRAIN (*Ann. Agron.*, 1898, 24, 130—134).—As bearing on the results of Schneidewind, who found that the pentosans present in straw may serve as food for denitrifying bacteria, an experiment is described in which the effect of adding starch and straw respectively to soil containing nitrates was observed. Whilst the addition of starch caused practically the whole of the nitrates to disappear, only about a third of the nitric nitrogen was lost under the influence of straw. The amount of straw was 1 per cent. of the weight of the soil, a quantity greatly in excess of the weights usually applied in practice. The injurious effect of great quantities of farmyard manure is perhaps due rather to nitrification being checked than to actual loss of nitrates.

It is agreed that fresh farmyard manure, like straw itself, contains denitrifying organisms, but inasmuch as their action is only evident when excessive amounts of manure are applied, it is unnecessary to incur the expense of treating stable-manure with sulphuric acid or superphosphate, either to prevent denitrification in the soil, or to prevent loss of nitrates in the manure itself, since nitrates do not seem to occur in farmyard manure. Application of acid to prevent loss of ammonia is, of course, quite another matter. N. H. J. M.

Changes which the Phosphoric Acid of Superphosphates and of Basic Slag Undergoes in the Soil. By ST. SMORAWSKI and H. JACOBSON (*Ann. Agron.*, 1898, 24, 292—293; from *Blatt. f. Zucker-rübenbau*, 1897, 232. Compare Abstr., 1897, ii, 120).—Phosphoric acid (1 and 0.5 per cent.), in the form of superphosphate and basic slag respectively, was mixed with soil poor in phosphates and extracted during 24 hours with water saturated with carbonic anhydride. The two manures behaved in exactly the same way as in the previous experiments. N. H. J. M.

Alkali Chlorides in the Grapes and Wines of the Province of Oran. By EDMOND BONJEAN (*Compt. rend.*, 1898, 126, 1275—1277).—Twenty-eight samples of wine were collected by the author in different parts of the province of Oran, especially in the neighbourhood of the salt lakes, and only 3 were found to contain less than 0.60 gram of chlorine per litre; 15 contained from 0.60 to 1.2 gram, and 10 contained more than 1.2 gram per litre. The maximum amount found was 4.5 gram per litre. There seems to be no general law as

to the distribution of the chlorine between sodium and potassium, but both metals were present in each case.

It is evident that great care is needed in forming an opinion as to the purity of a wine from the proportion of chlorine that it contains.

C. H. B.

Mangel-wurzel. By G. PATUREL (*Ann. Agron.*, 1898, **24**, 97—123).—Comparative experiments with different varieties of roots showed that the French roots, probably owing to their greater leaf development, contain a greater percentage of dry matter than other varieties; they also contain the most sugar and proteids.

The relation between the dry matter and the density of the juice is nearly constant ($\text{dry matter} \div \text{density} = 2.8$), so that the amount of dry matter, and hence the value of a crop, may be estimated by determining the sp. gr. of the expressed juice.

Roots which contain the lowest percentage of dry matter contain the largest amount of potassium nitrate; the French roots are poorest in nitrate, the German roots the richest.

As regards the yield per acre, the German varieties gave the heaviest crops but the smallest amount of dry matter. As a rule, the yield of sugar and proteids follow the yield of dry matter. The relation ($\text{sugar} + \text{nitrogenous matter} \div \text{dry matter}$) is highest in the French varieties. The relation $\text{nitric nitrogen} \div \text{total nitrogen}$ is very variable, from 8 to 17 in French to 35 and 40 in German roots. Six varieties of English roots held an intermediate position in value between the French and German varieties.

N. H. J. M.

Sesame. By AUGUST HEBEBRAND (*Landw. Versuchs-Stat.*, 1898, **51**, 45—81).—The following analyses of sesame seed, (1) white and (2) black East Indian, (3) Levantine, are given.

	Total	Proteid	Amide	Crude	Free	N-free	Pento-	Crude	
	Water.	nitrogen.	nitrogen.	nitrogen.	fat.	extract.	sans.	fibre.	Ash.
					acids.				
1.	5.42	3.63	3.46	0.17	52.75	1.64	6.30	4.69	2.88 5.27
2.	6.50	3.48	2.93	0.55	51.40	1.69	8.44	4.74	1.70 5.45
3.	5.25	3.11	3.04	0.07	56.75	1.58	6.04	4.69	3.71 4.07

The free fatty acids are calculated as oleic acid. The digestible nitrogen is (1) 3.35, (2) 3.13, and (3) 2.86 per cent.; the iodine number (1) 105.5, (3) 102.1.

The free oxalic acid and soluble oxalates were determined by extracting the acids, freed from fat, with water, adding acetic acid, and precipitating with calcium chloride. The phosphoric acid was determined in the ignited precipitate, and the corresponding amount of calcium phosphate deducted.

Insoluble oxalates were determined by digesting the powdered seeds (free from fat), first with a little dilute hydrogen chloride, and then for an hour on a water bath with strong aqueous sodium hydroxide. The filtrate was treated with excess of acetic acid and precipitated with calcium acetate. The precipitate was boiled with dilute acetic acid, ignited, and weighed. A correction was made after determining the phosphoric acid. The following percentage results

were obtained. Soluble oxalic acid (1) 0.131, (2) 0.256, (3) 0.080. Calcium oxalate (1) 1.821, (2) 1.229, (3) 0.210.

The white seeds contained 0.7635 per cent. of lecithin, and the following amounts of ash constituents (per cent. in the pure ash).

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ and Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
11.85	1.79	35.14	12.88	3.04	30.82	0.89	3.04	0.16

Analyses of sesame oil and cake are also given. The amount of fatty acids in the cake varies with the age of the samples. Cake which had been kept about 2 months contained on the average 80.9 per cent. of acids (in the fat), whilst samples kept for 1 month contained 66.9 per cent. The amount of acid is thus no criterion of the quality of a cake, and a high percentage does not indicate that the cake is old. Cake should not be broken or ground until just before it is used for feeding.

A list of references to other work on the subject is given.

N. H. J. M.

Nitrogen in the Vegetation of Forests. By ED. HENRY (*Ann. Agron.*, 1898, 24, 138—140; from *Compt. rend. Soc. Sci. Nancy*).—In agricultural soils, there is loss of nitrogen, in the form of nitrates, through removal in crops and in drainage. In the case of forests, there is presumably no loss of nitrates in drainage, since Boussingault, Ebermayer, Bréal, and the author failed to detect nitrates in forest soils. It is probable, however, that nitrification does take place in such soils, but that, as nitrates are produced, they are at once denitrified.

The gain of nitrogen which is known to take place in forest soil is attributed, on the one hand, to fixation of free nitrogen by leguminous plants (broom, gorse, &c.), and, on the other, to fixation by dead leaves.

It was found that when dead oak leaves were kept for a year in boxes exposed to air, the percentage of nitrogen in the dry matter rose from 1.108 to 1.923. Taking into account that there was at the same time a loss of 21.62 per cent. of dry matter, the percentage of nitrogen at the end of the year would have been 1.508, supposing the loss to have been entirely due to decomposition of non-nitrogenous matter. On the assumption that 3300 kilos. of dead leaves fall on a hectare, there would be a gain of 22 kilos. of nitrogen.

DEHÉRAIN calls attention to the results obtained by Kostycheff (*Abstr.*, 1891, 611), indicating that the gain of nitrogen is only relative, being due to disappearance of carbonaceous matter. N. H. J. M.

Results of Vegetation Experiments for ascertaining the Manurial Requirements of Soils. By MAX MAERCKER (*Jahrb. agrik.-chem. Versuchs-Stat. Halle a.-S.*, 1896, 2, 169—173).—In order to ascertain by direct experiment what manures were wanted, white mustard was grown in the soil, in pots, without manure, with nitrogen and phosphoric acid, separately, together, and in conjunction with potash, and with potash and calcium carbonate. The following results, obtained with three samples of soil from a farm which had

been much exhausted by the growth of fodder crops, are of interest, as giving clear indication of deficiency of phosphoric acid. The amounts of manure applied were: N, 3·0; P_2O_5 , 1·5; CaO, 3·0 grams. The numbers indicate the amount of produce.

	N.	N + P_2O_5 .	N + CaO.	N + P_2O_5 + CaO.
1. Heavy loam	18·8	54·3	21·5	55·6
2. Mild „	35·0	67·6	41·0	63·1
3. Sandy „	65·6	58·8	60·4	60·4

Deficiency of nitrogen was not expected, as plenty of cattle were kept. Making allowance for the fact that in pot experiments much greater crops and, in consequence, much greater differences in amounts of produce are obtained than in the field, it may be safely assumed that in the case of soils 1 and 2 an abundant application of phosphates would have a very decided effect. In the case of soil No. 3, there was no indication of a deficiency of phosphates.

Analyses of the three soils showed high percentages of phosphoric acid (0·230, 0·264, and 0·253), which, in the case of the first two, were not at all in accordance with the results of the vegetation experiments. The fact that soil No. 3 contained only about the same amount of phosphoric acid as 1 and 2, whilst, unlike these, it did not show a deficiency in the pot experiments, accords with the author's observation that the phosphoric acid of sandy soils is much more readily available than in loam or clay soils.

Estimation of total phosphoric acid in soil is, therefore, of very limited value; whilst a low percentage indicates a deficiency, a high percentage is no conclusive evidence that available phosphoric acid is not deficient. At present, vegetation experiments cannot be dispensed with.

N. H. J. M.

Loss of Ammonia in the Production of Farmyard Manure. By PIERRE P. DEHÉRAIN (*Compt. rend.*, 1898, 126, 1305—1310).—It has been shown by Berthelot and André that ammonium carbonate dissociates in aqueous solution, the escape of the ammonia being determined and regulated by that of the carbonic anhydride. These results are found to be applicable to the loss of ammonia in the formation of manure, a loss amounting usually to one-third, sometimes to one-half, of the total nitrogen contained in the excreta. Conditions favouring the escape into the atmosphere of the carbonic anhydride formed by the fermentation are accompanied by loss of ammonia, whilst when fermentation takes place in an atmosphere of carbonic anhydride, no loss of ammonia occurs. The author deduces from his observations the following practical rules. The soiled litter should be transferred to the dung-heap as frequently as possible, and the stable gutters flushed with water to carry the liquid excreta into a tank, which also receives the drainings of the dung-heap. The latter should be well heaped up and often watered with the liquid from the tank; an active fermentation is thus maintained, and the constant production of carbonic anhydride prevents the escape of ammonia.

N. L.

Wiborgh Phosphate, a Manure prepared from Gellivara Apatite. By LARS F. NILSON (*Bied. Centr.*, 1898, 27, 385—390; from *Kongl. landbruksakad. handl. tidskr.*, 1898, 1—17).—The magnetite found at Grängesberg and Gellivara is, in part, mixed with considerable amounts of apatite. To separate the two substances, the mineral is crushed until grains of about 1 mm. are obtained, and the iron compounds are then separated magnetically. The iron ore then contains about 71 per cent. of iron with very little phosphate, and is very suitable for the Martin process. The refuse contains about 80 per cent. of apatite, the rest being mainly felspar, with some quartz, mica and non-magnetic ferric oxides.

As, at the present time, there is little prospect of this substance being utilised as basic slag, a process, suitable for all crude phosphates, has been proposed by Professor Wiborgh for converting it into manure, which consists in heating the product with sodium carbonate at about 900—1000°. A sample of Wiborgh phosphate thus prepared contained: K_2O , 1.54; Na_2O , 14.69; CaO , 38.12; MgO , 2.88; Fe_2O_3 and Al_2O_3 , 4.50; P_2O_5 , 27.01; SiO_2 , 9.99; SO_3 , 0.27; F and loss on ignition, 1.00 per cent. It dissolves completely in hydrochloric acid, but only very slightly in water. The citrate-solubility of the phosphoric acid is readily brought up to 95 per cent. In preparing the phosphate, the best results are obtained with 30 parts of sodium carbonate to 100 parts of apatite, when the latter contains 17 per cent. of felspar. Without felspar, the apatite is much less readily attacked and the product contains much less citrate-soluble phosphoric acid.

A number of pot experiments were made with oats, peas, and sugar beet, in which different amounts of the new phosphate were compared with corresponding amounts of citrate-soluble phosphoric acid in the form of basic slag and superphosphate respectively. In the case of oats, Wiborgh phosphate and basic slag were about equal, and better than superphosphate. With peas, all three phosphates gave about the same amount of grain, but basic slag produced the most straw. As regards sugar beet, the percentage of sugar in the roots was about the same with Wiborgh phosphate as with basic slag, when large amounts were applied.

N. H. J. M.

Decomposition of Milk-Fat during the Ripening of Cheese. By H. WEIGMANN and A. BACKE (*Landw. Versuchs-Stat.*, 1898, 51, 1—14).—Previous results obtained by Henzold and Weigmann showed that, in the ripening of cheese, the greater portion of the milk fat remains unchanged, whilst according to Weidmann (*Abstr.*, 1882, 692) the fat is either not altered at all or only very slightly (compare also Manetti and Musso, *Landw. Versuchs-Stat.*, 1878, 21, 218). Duclaux concluded that the fat undergoes only a slight change at first, but that subsequently the change is very great, and that whilst at first the change is limited to the glycerides of the soluble fatty acids, the oleic acid glyceride is afterwards attacked (*Principes de laiterie*).

The examination of a number of different kinds of cheese showed that, in the process of ripening, a portion of the fat is decomposed. In cheeses of ordinary ripeness, 1—7 per cent. of the fat consists of non-

volatile fatty acids. Of the hard cheeses, the newest ($2\frac{1}{2}$ months) contained the smallest amount of fatty acids, whilst a soft cheese (3 months) was found to contain nearly 7 per cent., indicating that the decomposition depends more on the intensity of the ripening than on the age. There is also an indication that even after $2\frac{1}{2}$ months the decomposition may extend to the glycerides of the non-volatile fatty acids.

The following is the method employed. The cheese, mixed with sand, was extracted with ether, the dry extract purified by dissolving in light petroleum, and again dried at 100° to 105° . The free fatty acids were obtained by exactly neutralising the light petroleum extract, dissolved in ether and alcohol, with N/10 caustic soda, after titrating a portion in order to ascertain the amount of alkali required. Any unchanged fat was then removed by extracting with light petroleum as long as anything dissolved; finally, the alcohol was evaporated, the residue treated with dilute sulphuric acid, and the liquid fatty acids removed from the surface. The acids were weighed, the melting point determined, and in some cases they were titrated with caustic soda.

N. H. J. M.

Analytical Chemistry.

Volumetric Analysis: Correction to be applied when an Aliquot Part of a Filtrate is Titrated. By RUOSS (*Zeit. anal. Chem.*, 1898, 37, 422—426).—In cases where a substance is estimated by adding a known excess of a precipitant, making up to a known volume, filtering through a dry filter, and titrating the excess of precipitant in a portion of the filtrate, the error $(\bar{X} - x)$ arising from neglecting the volume of the precipitate amounts to $\frac{arx}{1000 sm - ar}$, where \bar{X} is the true amount of the precipitate obtained, $x = a(C - r)$, the amount calculated without applying the correction, $a = \frac{\text{equivalent of precipitate}}{\text{equivalent of precipitant}}$, s = sp. gr. of precipitate, m , volume to which the mixture is made up, C , the amount of precipitant used, and r , the excess found, calculated on the total volume m . Since, however, ar is small compared with $1000 sm$, it may be omitted from the denominator without appreciable error, and $x + \frac{arx}{1000 sm}$ is the corrected result. By making $m = 50$ c.c., and using 25 c.c. of filtrate for titration, any error in this operation is only multiplied by 2, and by keeping the excess of the precipitant small, the correction often amounts to only a few tenths of a milligram. M. J. S.

Spectrum Analysis of Minerals. By ARNAUD DE GRAMONT (*Compt. rend.*, 1898, 126, 1513—1515).—The author has applied to a large number of compounds his method of allowing a condensed spark

to impinge on a bead of a mineral or precipitate previously powdered and fused with sodium carbonate. Lithium is very readily recognised by means of the red line 6708 and the orange line 6104. Sodium is recognised by the red doublet and the less refrangible green doublet, but potassium is difficult to recognise, the green group K_{α} and the violet line 4046 being the most distinct. Rubidium is easily recognised by means of the violet lines 4216 and 4202, and caesium by its blue lines 4593 and 4556.

Barium, calcium, and strontium are particularly easily detected by this method; the first by the red and orange lines 6497 and 6142, the green 5778, 5536, and 4934, and the blue 4554; the second by the blue lines 4455, 4435, 4426, and especially by the violet 4227 as well as the ultra-violet 3969 and 3934; the last by the blue line 4608, the indigo 4306, and the violet 4216. Magnesium under these conditions is characterised by the green triplet Mg_{α} , beryllium by the blue line 4573, the reaction being less sensitive than with magnesium, manganese by the group of five blue lines Mn_{α} , chromium by the green triplet 5209, 5206, and 5205. Iron and nickel should not be sought for by this method. Aluminium, however, is readily detected by means of the red doublet 6245, 6235, provided that lithium carbonate is used instead of sodium carbonate. Vanadium shows the strong indigo lines, especially 4408, and zirconium shows five lines in the blue between 4816 and 4690, the line 4740 being the strongest and most persistent.

The author gives the results of the examination of a large number of minerals by this method.

C. H. B.

Stereoelectrolysis of Minerals. By FRANÇOIS MAYENÇON (*C.R. Assoc. Franç. Adv. Sci.*, 1898 [1897], 26, [ii], 347—348).—The name stereoelectrolysis is given to the following method of analysing minerals. The fine powder is made into a paste with water, placed between two pieces of filter paper, and electrolysed between platinum electrodes with six dichromate cells. Metals or their oxides appear at the cathode, and acid radicles at the anode. For example, with galena, metallic lead and sulphuric acid are obtained, and with barytes, baryta and sulphuric acid. The separated constituents are then identified by ordinary analysis.

L. J. S.

Detection of Perchlorate in Chili Saltpetre. By HEINRICH FRESSENIUS, and H. BAYERLEIN (*Zeit. anal. Chem.*, 1898, 37, 501—504).—The authors describe their method of carrying out Behren's test (this vol., ii, 482), and claim that as small a proportion as 0.2 per cent. of perchlorate can be directly detected, thus avoiding the somewhat troublesome concentration by means of alcohol recommended by Breukeleveen. Four to six drops of a concentrated, filtered solution of the substance are placed on a microscopic slide, a few crystals of rubidium chloride are added, and the solution is coloured distinctly pink with permanganate. It is then evaporated over a small flame until a crystalline crust about 4 mm. broad forms round the edge of the liquid, when it is transferred to the stage of a microscope with a magnifying power of 150. Should the proportion of perchlorate be very small, further evaporation will be necessary

before the violet-red crystals make their appearance. The paper is illustrated with drawings of the appearance under the microscope.

M. J. S.

Detection of Bromine in Urine. By ADOLF JOLLES (*Zeit. anal. Chem.*, 1898, 37, 439—440).—The urine (10 c.c.) is mixed with sulphuric acid and excess of permanganate in a narrow-necked flask. A piece of filter paper soaked in a 0.1 per cent. solution of para-dimethylphenylenediamine is placed in the neck, and the flask is warmed on the water bath. If bromine is present, the paper acquires a violet colour, passing at the edges through blue into grey and brown. As little as 0.1 milligram is easily detected. Neither chlorine nor iodine (unless in enormous excess) interferes with the reaction.

M. J. S.

Special Cases of the Estimation of Sulphur and of Iodine. By ANTONIO LONGI and L. BONAVIA (*Gazzetta*, 1898, 28, i, 336—341).—The authors propose the following methods for estimating, in the same solution, sulphur, in the form of sulphites, thiosulphates, trithionates, tetrathionates, sulphides or polysulphides, and iodine, in the form of iodide or iodate.

A. The solution containing sulphur and iodine is made alkaline with potassium carbonate, oxidised with potassium permanganate (the excess of the latter being destroyed by alcohol) acidified with acetic acid, and filtered; one proportional part of the filtrate is precipitated with barium chloride and the barium sulphate weighed, whilst another is treated with potassium iodide and the iodine titrated with thio-sulphate, after acidification with hydrochloric acid. If the solution contains no chlorides, it is treated, after oxidation and filtration, with nitric acid free from nitrous acid at 50—60°, and precipitated with barium nitrate; after filtering off the barium sulphate, the iodine is determined in the filtrate as before.

B. The solution of sulphur and iodine compounds is oxidised with sodium peroxide, the excess of the latter decomposed, and the iodic acid reduced with zinc dust; the filtrate may be treated in two ways. *a.* It is acidified with acetic acid, precipitated with barium acetate, and the barium sulphate filtered off after several hours repose at 40°; the iodine is precipitated in the filtrate with silver nitrate. *b.* It is neutralised with nitric acid, precipitated with silver nitrate, and strongly acidified with nitric acid; the filtrate from the silver iodide is precipitated with barium nitrate.

The several methods described all gave satisfactory test results.

W. J. P.

Separation of Dithionic Acid from the other Acids of Sulphur. By ANTONIO LONGI and L. BONAVIA (*Gazzetta*, 1898, 28, i, 341—344).—Salts of sulphur acids of a lower degree of oxidation than sulphuric acid are, with the exception of dithionic acid, oxidised to sulphuric acid in alkaline solution by potassium permanganate or hypobromite; after the oxidation, the solution is precipitated with barium acetate, and the barium sulphate filtered off and weighed. The dithionic acid in the filtrate is oxidised to sulphuric

acid by digestion for several hours with nitrohydrochloric acid or potassium chlorate and hydrochloric acid in presence of barium chloride; the separated barium sulphate is then collected and weighed.

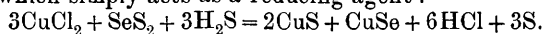
The test analyses are very satisfactory.

W. J. P.

Selenium and Tellurium. By EDWARD KELLER (*J. Amer. Chem. Soc.*, 1897, 19, 771—778).—The precipitation of selenium and tellurium from solutions of the corresponding selenous and tellurous acids by sulphurous anhydride is only complete in the presence of hydrochloric acid. Selenium appears to be completely precipitated only when the solution contains 30 per cent. or more of strong hydrochloric acid of sp. gr. = 1.175, whereas tellurium is completely thrown down from solutions containing 10 per cent. of this acid, but is not completely removed when the percentage of this acid present rises above 60.

The two elements are both precipitated when a ferric salt is added to solutions of selenous and tellurous acids and the iron precipitated with ammonia, but precipitation is only complete when a considerable excess of iron is present.

Selenium may be separated from tellurium by means of ferrous sulphate, which reduces selenous acid completely in acid solution, but has no action on tellurous acid. Selenium cannot be separated from copper by treatment of the mixed sulphides of these elements with sodium sulphide, since the residue left invariably contains some selenium. Quantitative experiments lend some probability to the idea that this precipitate contains copper selenide formed by the action of selenium sulphide on cupric chloride in the presence of hydrogen sulphide, which simply acts as a reducing agent:



A. H.

Modified Form of Nitrometer for Use in Nitrogen Estimations by the Absolute Method. By HOOPER A. D. JOWETT and FRANCIS H. CARR (*Chem. News*, 1898, 78, 97).—In this nitrometer the two limbs are continuous below, as in the Schwarz apparatus, but with a three-way cock between them, which can put the measuring tube in connection either with a nozzle or with the pressure tube; the latter when taking readings, the former during a combustion, so that the unabsorbed gas expels potash by the nozzle, which then dips under potash in a dish. The measuring tube is fitted with a side tube for admitting gas at the lower end, and with a two-way cock above for connecting with an outlet for the withdrawal of gas for analysis, or with a funnel for the admission of potash, a gentle stream of which is allowed to flow through the apparatus during a combustion.

D. A. L.

New Method of Estimating Nitric Acid. By E. BOHLIG (*Zeit. anal. Chem.*, 1898, 37, 498—501).—The proposed method is very suitable for the estimation of nitrates in natural waters. The dry residue from 100 c.c. of the water evaporated in a conical flask, is treated with a few c.c. of concentrated sulphuric acid, and the neck of the flask immediately closed by a caoutchouc stopper, through which pass two short glass tubes of equal length. The other ends of these tubes

are similarly fitted into another caoutchouc stopper, which is pushed loosely into the neck of a second conical flask containing a known excess of potassium ferrocyanide in 80—100 c.c. of water, the position of the two flasks being horizontal. The sulphuric acid is then caused to moisten the whole of the water-residue, and as soon as evolution of gas ceases, the stopper is tightened in the neck of the second flask, and the apparatus placed vertically. The liberated nitric and hydrochloric acids (the presence of a sufficient amount of chloride being presupposed or provided for) react with the ferrocyanide thus, $2\text{HNO}_3 + 6\text{HCl} + 6\text{K}_4\text{FeCy}_6 = 3\text{K}_6\text{Fe}_2\text{Cy}_{12} + 4\text{H}_2\text{O} + 6\text{KCl} + \text{N}_2\text{O}_2$. The contents of the flasks are thoroughly mixed by repeatedly inverting the apparatus, so as to allow the liquid in the upper flask to run into the lower one, and when the free chlorine is completely absorbed, the unoxidised ferrocyanide is titrated by permanganate. The organic matter usually present in a water residue reduces permanganate so much more slowly than does hydroferrocyanic acid that it does not interfere with the recognition of the end point.

M. J. S.

Laboratory Notes. By W. F. KEATING STOCK (*J. Soc. Chem. Ind.*, 1897, 16, 107—108).—*Extraction of soluble phosphates from artificial fertilisers.*—The following method is recommended for the analysis. From 20 to 30 grams of the fertiliser is thoroughly shaken, after the addition of 20 to 30 ordinary glass marbles, with from 2 to 3 litres of water in a closed bottle during 3 hours; the liquid is then allowed to clear by subsidence, or if this takes place slowly, is filtered, and an aliquot portion withdrawn for analysis.

Estimation of nitric nitrogen in water analysis.—The following method gives good results, and has the advantage that the copper-zinc couple can be used repeatedly during several months. A 7 oz. wide-mouthed stoppered bottle is nearly filled with copper-zinc prepared in the usual manner, and 100 c.c. of the water to be analysed added; the stopper is then inserted, and the mixture left at 20—25° during 48 hours; after thoroughly shaking the bottle, 50 c.c. of its contents is withdrawn, 200 c.c. of water free from ammonia is added, and the mixture distilled with sodium carbonate according to the ordinary method.

Extraction apparatus.—In this apparatus, the substance to be exhausted is contained in a tube surrounded by the vapours of the boiling solvent; the latter thus acts at its boiling temperature, and consequently, very economical results are obtained.

W. A. D.

Estimation of Phosphoric Acid in Superphosphates. By LÉO VIGNON (*Compt. rend.*, 1898, 126, 1522—1523).—In the analysis of superphosphates, it is customary to estimate separately and directly the quantities of phosphoric acid soluble in water and ammonium citrate solution respectively. The author finds, however, that when the quantity of phosphoric acid soluble in the citrate solution is small, the results are almost invariably too low, even when the precipitation is allowed to go on for several hours. If, however, the aqueous solution and the ammonium citrate solution are mixed, the estimation of the total phosphoric acid in them is accurate. It is therefore recommended to estimate separately the phosphoric acid soluble in

water, and the phosphoric acid in the mixed aqueous and ammonium citrate solutions, and to determine by difference the quantity of phosphoric acid soluble in the ammonium citrate solution. C. H. B.

Analysis of Bone Superphosphate. By F. POQUILLON (*Chem. News*, 1898, 78, 3—4).—The usual determinations of the soluble phosphoric acid and the nitrogen are not considered adequate for ascertaining whether the sample is an admixture of ordinary superphosphate and nitrogenous matter, or a genuine bone superphosphate. It is suggested that the amount of fatty matter soluble in carbon bisulphide or in benzene should also be estimated, inasmuch as the proportional relation of that factor to the phosphoric acid is practically constant in bone superphosphates, being 10 to 12 of fat to 100 of phosphoric acid in superphosphates from green bones or degelatinised bones, with fat previously removed by water, and 6.5 to 100 in superphosphates from bones from which the fat has been extracted by benzene, proportions that cannot conveniently be obtained by admixture with ordinary superphosphate when the nitrogen is also taken into consideration. D. A. L.

Estimation of Boric Acid. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1898, 28, i, 344—348).—The author has shown (*Real. Accad. Linc.*, 1889, [iv], 6), that Gooch's method (*Abstr.*, 1887, 299) is the best for the estimation of boric acid; Thaddéeff (*Abstr.*, 1897, ii, 597) does not quote this paper, and gives a method for determining boric acid which is inconvenient and complicated. Gooch's method is the only direct and convenient one for determining boric acid. W. J. P.

Action of Carbonic Anhydride on Soluble Borates. By LOUIS C. JONES (*Amer. J. Sci.*, 1898, 5, 442—446).—Morse and Burton have worked out a process for estimating boric acid based upon the assumption that when a solution of this acid, mixed with excess of barium hydroxide is treated with carbonic anhydride, the excess of barium only is precipitated as carbonate. The author, having made several experiments, finds the process quite untrustworthy, as the barium borate is also partially decomposed.

Carbonic anhydride is capable of entirely displacing the boric acid, even from borax, if the acid is removed as fast as it is liberated. If a borate is boiled with methylic alcohol in a suitable apparatus through which a current of carbonic anhydride is being passed, the residue will, after some time, give no reaction for boric acid, the whole of it having volatilised with the alcohol. L. DE K.

Detection and Estimation of Carbonic Oxide in Air in presence of traces of Gaseous Hydrocarbons. By ARMAND GAUTIER (*Compt. rend.*, 1898, 126, 1299—1305. Compare this vol., ii, 535—538).—The air, previously filtered through glass wool and freed from carbonic anhydride and aqueous vapour by means of caustic potash, barium hydroxide, and phosphoric anhydride, is passed successively through two tubes heated in an air bath at 100—105°, and containing respectively iodic anhydride and finely divided metallic copper. The carbonic oxide is oxidised by the iodic anhydride with liberation of iodine, the latter being completely absorbed by the

copper, which is weighed before and after the experiment. Each milligram of iodine corresponds with 0.441 c.c. of carbonic oxide. In the presence of hydrocarbons of the ethylene and acetylene series, which also reduce iodic anhydride to some extent, the air, after passing over the heated copper, is passed through weighed tubes of phosphoric anhydride and barium hydroxide to absorb the water and carbonic anhydride formed by the oxidation of the carbonic oxide and hydrocarbons. The tube containing iodic anhydride is also weighed before and after the experiment. The loss in weight of the latter, less the iodine absorbed by the copper, gives the oxygen supplied by the iodic anhydride, and the difference between this and the amount of oxygen corresponding with the water and carbonic anhydride produced, gives the weight of oxygen contained in the carbonic oxide originally present in the air.

N. L.

Sources of Inaccuracy in the Estimation of Carbonic Anhydride and Aqueous Vapour in Large Volumes of Air. By ARMAND GAUTIER (*Compt. rend.*, 1898, 126, 1387—1393).—The author's researches on the estimation of minute quantities of carbonic oxide and hydrocarbons in the atmosphere (this vol., ii, 536) have led him to reconsider the question of the preliminary purification of the air from carbonic anhydride and aqueous vapour, and the relative efficiency of caustic potash, barium hydroxide, sulphuric acid, and phosphoric anhydride is discussed in detail. Even after the most careful purification by means of caustic potash, air still retains carbonic anhydride to the extent of about 0.1 c.c. per 100 litres, but this is easily removed by passing the gas through baryta water, or through a tube containing crystals of barium hydroxide slightly moistened with water. Experiment shows that the traces of carbonic anhydride which escape the action of caustic potash are not to be attributed to oxidation of the rubber connections of the apparatus, or to diffusion, through the latter, of the external air.

The removal of aqueous vapour may be effected, with sufficient accuracy for most purposes, by means of sulphuric acid; 100 litres of air, carefully dried by this reagent, were found to retain only 0.3 to 0.353 milligram of water, as estimated by absorption by phosphoric anhydride. Since, however, sulphuric acid dissolves carbonic anhydride and other gases, it is preferable, in the most exact analyses, to use phosphoric anhydride. Experiments were made with a view of ascertaining whether the volatility of sulphuric acid is an appreciable source of inaccuracy. One hundred and ninety-two litres of air, after being dried with sulphuric acid, and subsequently filtered through glass wool, produced no sensible turbidity in baryta water, but the latter, on evaporating with hydrochloric acid and taking up the residue with water, left 0.1 milligram of barium sulphate, corresponding to 0.00022 milligram of sulphuric acid per litre of air, a quite insignificant proportion. It is calculated, from this result, that the vapour pressure of sulphuric acid at 13—14° does not exceed one twenty-millionth of an atmosphere.

N. L.

Table for Calculating Potassium Platinochloride into Potassium Oxide. By GÖLTSCHE (*Zeit. anal. Chem.*, 1898, *supp.*).—This table gives the weight of potassium oxide equivalent to

potassium platinochloride for every half milligram of the latter up to 1 gram. The coefficient 0.19308 was used in the calculation.

M. J. S.

Estimation of Calcium. By MAX PASSON (*Zeit. angew. Chem.*, 1898, 776—777).—The advantage of this process is that it may be used in the presence of iron, alumina, magnesia, and phosphoric acid without their previous removal.

The sample is boiled with dilute nitro-hydrochloric acid in a half-litre flask until everything but the sand is dissolved. When cold, the liquid is made up to the mark, and an aliquot part is slightly over-neutralised with dilute ammonia, using phenolphthalein as indicator; a 10 per cent. solution of citric acid is then added until the precipitate has completely redissolved, and after that another 10 c.c. of the citric acid solution. The liquid, diluted to about 200 c.c., is heated to boiling, precipitated with ammonium oxalate, and the precipitate, which is crystalline, is collected, washed, ignited, and weighed as calcium oxide. The test analyses show the great accuracy of the process. L. DE K.

Cyanometric Estimation of some Metals. By HARRY BREARLEY and HORACE JERVIS (*Chem. News*, 1878, 78, 177—179, 190—191. Compare this vol., ii, 258).—In adopting this method, to ensure uniformity, either direct titration, or adding excess of cyanide and titrating back with silver nitrate should be exclusively adopted, moreover, the quantity of potassium iodide present affects the changes, and should be regulated; 2 c.c. of a 2 per cent. solution for each 500 c.c. of solution titrated gives the deepest desirable cloudiness.

Nickel and copper present contrasts in their behaviour in this process; nitrates, acetates, tartrates, and sulphates in alkaline solution interfere in the case of copper, but not in that of nickel; with the latter metal, too, the reaction is complete with the theoretical quantity of cyanide, whilst with the former metal a great excess is required. In titrating nickel, an error may arise by the formation of a silky, crystalline compound, which is, however, prevented by the use of ammonium sulphate. Various experiments show that chromic oxide, aluminium, zinc, and iron interfere to a noticeable extent with the estimation of nickel by this method, zinc raising, the others lowering, the result, whereas calcium, barium, strontium, magnesium, cadmium, manganese, chromic acid, tin, molybdenum, arsenic, antimony, bismuth, lead, uranium, and tungsten do not interfere. This is true when the amount of nickel is 0.1 gram, the amount of interfering metal 0.05 and 0.1 gram, and the excess of ammonia 10 c.c. of 2N solution, the foreign element being generally added as chloride, and ammonium chloride replacing the sulphate where insoluble sulphates would be formed. The interference of *zinc* decreases with increased excess of ammonia, and may be obviated by adding the cyanide to a faintly acid or neutral solution, and using sodium carbonate instead of ammonia; then filtering, adding silver nitrate to the filtrate until only traces of free potassium cyanide remain, then re-passing through the same filter and completing the filtration; if cadmium is present in quantity sufficient to interfere, the same method should be used. Whilst recognising the

utility of sodium pyrophosphate as a corrective in the case of zinc, the authors consider that the benefit observed is due to the low results arising from this corrective compensating the high result due to the zinc (Moore, Abstr., 1889, 1033) and, as Moore found with iron, the authors find with aluminium, that sodium pyrophosphate is not a good reagent to use for preventing precipitation; it is, however, useful for the purpose in the case of copper titrations. Tartaric acid may be used to keep aluminium in solution, 0.1 gram of this metal requiring 1 gram of the acid, a large quantity of which, however, delays the reaction. In the presence of *aluminium*, the titration of nickel may be accurately effected by proceeding as in the presence of zinc, but adding the usual excess of ammonia, and not sodium carbonate, filtering an aliquot portion of the liquid, and going back with silver nitrate; a preliminary quantitative test, or some knowledge of the amount of nickel present, is necessary. In the case of *iron*, the low result is due to mechanical retention of the nickel by the precipitate, and is overcome by adding the cyanide before rendering the solution alkaline, or by using an alkali carbonate instead of ammonia for precipitation. If any interference is anticipated on account of *manganese*, the treatment as in the case of zinc may be followed, using ammonium carbonate, or ammonium chloride may be used to keep the manganese in solution, but, as a matter of fact, the precipitated manganese hydroxides are harmless. In the presence of *chromium*, the direct titration of nickel is inadmissible; but with a knowledge of the approximate amount of nickel present, adding excess of cyanide, allowing some time to elapse and then titrating back, it yields fairly accurate results; better still, the excess of cyanide may be added before making the solution alkaline. The mixed solution of chromium and nickel salts, when neutralised, changes from greenish-blue to full green, the blue is restored by a drop of hydrochloric acid and the titration proceeded with; sometimes a precipitate forms before all the cyanide is added, if small it does not interfere. Chromic oxide salts may be rendered harmless by transforming them into chromates, and using ammonium sulphate to retain any basic nickel chromate in solution. *Tin* should be in the stannic form. In the presence of *sodium molybdate*, the titration should not be delayed, inasmuch as a nickel molybdenum precipitate forms very slowly; its formation may be further retarded by using ammonium sulphate. For similar reasons, the titration should not be delayed in the presence of *arsenic*; sodium arsenite lowers the results, but only by less than 1 per cent.; with the arsenate, however, the results are accurate. *Antimony* and *bismuth* oxychlorides do not interfere, but their precipitation may be prevented by means of a small amount of tartaric acid. *Lead* acetate does not interfere, and precipitation may be avoided by using nitrates instead of sulphates to heighten the iodine turbidity. *Uranium* forms a precipitate with ammonia, so that the carbonate should be used. Citric acid causes low results, and cannot be used to replace tartaric acid. It is noted that adding the cyanide to the slightly acid solution does not occasion any serious loss; moreover, experiments indicate that the interference in the cases of chromium, aluminium, and iron appears to be due to mechanical retention. The case of manganese and copper is to be investigated.

D. A. L.

Volumetric Estimation of Lead, Copper, Iron, Potassium Ferrocyanide, Dextrose, and Sulphuric Acid (in Sulphates). By Ruoss (*Zeit. anal. Chem.*, 1898, **37**, 426—436).—The operations are best performed in test-tubes of about 120 c.c. capacity. The lead to be estimated is thrown down as sulphate, or ferrocyanide, by an excess of sodium sulphate or potassium ferrocyanide. After boiling and cooling, phenolphthalein is added, and the liquid is accurately neutralised in the cold. It is then heated to boiling, and standard barium hydroxide solution is run in from a burette until the red colour of the upper liquor does not disappear on boiling and is not increased in intensity by further additions. The red colour becomes permanent when half of the lead salt is converted into oxide, but it is better to add a few c.c. in excess and titrate back with N/5 acid. Conversely, sulphates and ferrocyanides are estimated by precipitating with lead nitrate and titrating the precipitate with baryta as above, after filtering and washing, if any metals precipitable by baryta are present.

Chromic acid may be estimated by precipitating with an excess of lead and titrating the lead in an aliquot part of the filtrate, correcting if necessary for the volume of the lead chromate (see this vol., ii, 635). For the estimation of copper, sodium oxalate is added until the copper oxalate first precipitated is redissolved, and then phenolphthalein and baryta. As soon as the free acid is neutralised, the solution acquires the colour of methyl-violet 6B. By adding calcium chloride, the double oxalate is decomposed, and now the red colour of the indicator does not appear until the copper is precipitated. A small excess of baryta is employed as in the case of lead, and the excess of alkali is titrated back with acid, but in this instance at the boiling point. Small quantities of copper can be estimated by precipitating as ferrocyanide, and titrating with baryta; the red colour appears when half the copper ferrocyanide is converted into oxide. The subsidence of all the ferrocyanide precipitates is greatly promoted by adding solid potassium nitrate and boiling.

A modification of the above method serves well for ascertaining the amount of cuprous oxide obtained in a sugar estimation. After proceeding as prescribed by Allihn, but with the sugar solution diluted 2½-fold, the precipitate with its filter is thrown into a test-tube, dissolved in the smallest possible quantity of nitric acid, and the solution boiled for 3 minutes. Soda solution (free from carbonate) is then added until (with phenolphthalein) there is a decided excess of alkali, which excess is then exactly removed by dilute sulphuric acid. To the still hot solution, 15 c.c. of N/2.5 sulphuric acid is added, together with methyl-orange, and after cooling, the excess of free acid is measured with N/5 soda. The greenish-yellow colour which indicates the termination of the titration can be very sharply recognised.

Ferric ferrocyanide, which has been washed with potassium nitrate solution until free from acid, can be titrated with baryta and phenolphthalein, the red colour appearing when all the iron is as hydroxide.

M. J. S.

Separations of Aluminium [from other Metals] by Hydrochloric Acid. By FRANK S. HAVENS (*Amer. J. Sci.*, 1898, **6**, 45—48).—The author (*Abstr.*, 1897, ii, 232) has published a very good process

for separating aluminium from iron and beryllium, based on the fact that its chloride is insoluble in a mixture of hydrochloric acid with its own volume of ether previously saturated with hydrogen chloride.

He now states that this process works equally well with mixtures of chloride of aluminium with chlorides of zinc, copper, mercury, and bismuth.

L. DE K.

Condition of Oxidation of Manganese Precipitated by the Chlorate Process. By FRANK A. GOOCH and MARTHA AUSTIN (*Amer. J. Sci.*, 1898, [iv], 5, 260—268).—The authors' experiments show that if due attention be paid to details, the precipitation of manganese nitrate by sodium chlorate in presence of concentrated nitric acid is practically complete, the manganese escaping precipitation being found in no case to exceed 0.0001 gram. The use of sodium chlorate is to be preferred to that of the potassium salt, since the latter, owing to its sparing solubility, is apt to be mechanically carried down with the precipitated oxide; sodium chlorate also has the advantage of being more easily decomposed. The "oxygen value" of the precipitated oxide is best determined by dissolving it in sulphuric acid and potassium iodide solution, and titrating the liberated iodine with standard sodium thiosulphate solution; or by reducing the oxide with N/10 arsenious acid solution in presence of sulphuric acid, neutralising the solution with potassium hydrogen carbonate, and titrating the excess of arsenious acid with standard iodine solution. In the latter process, sufficient tartaric acid or alkali tartrate should be added to the acid solution to prevent the precipitation of manganese during the subsequent neutralisation. If this precaution is not taken, errors may be introduced owing to the reoxidation of the precipitated manganous carbonate by the iodine. A series of analyses made by the methods just described showed that the precipitate obtained in the chlorate process contains less oxygen than corresponds with the degree of oxidation of manganese dioxide, and that the average error thus introduced into analyses based upon the assumption that MnO_2 is precipitated amounts to more than 2 per cent. The oxide may, however, be obtained of a definite and constant composition by a modification of the process, based upon the observation of Wright and Menke that by the action of a dilute solution of potassium permanganate, in presence of zinc sulphate, on manganous sulphate at 80° , an oxide is precipitated which, although combined with alkali, contains oxygen exactly in the proportion corresponding with the dioxide. Three-fifths of the manganese in the precipitate represents the amount originally present in the manganous sulphate. The following method of procedure is recommended.

The solution of the manganous salt is evaporated to dryness, heated with nitric acid until oxides of nitrogen are no longer evolved, and concentrated nitric acid then added until the volume of the liquid is 85 c.c. Sodium chlorate (5 grams) is added, the liquid boiled for 5 minutes, more nitric acid (15 c.c.) and a few crystals of the chlorate introduced, and the solution again boiled. After cooling, the precipitate is collected on an asbestos filter, washed with water, dissolved in 2 c.c. of hydrochloric acid, and the solution evaporated with 5 c.c.

of concentrated sulphuric acid until the hydrochloric acid is completely expelled. The solution of the manganous sulphate (containing not more than 0.5 gram of the salt) is nearly neutralised with potassium carbonate, mixed with solutions of zinc sulphate (2 grams) and potassium permanganate (1.5 grams), and the liquid, amounting to about 500 c.c., heated to 80°, and potassium hydrogen carbonate added in quantity rather more than sufficient to neutralise the acid still remaining. The precipitate is collected, washed with water, and its oxygen value determined by one or other of the methods described above. The results obtained by this process are very satisfactory. N. L.

Estimation of Manganese as the Sulphate and as the Oxide. By FRANK A. GOOCH and MARTHA AUSTIN (*Amer. J. Sci.*, 1898, 5, 209—214).—The authors state that the best way of estimating manganese is to weigh it in the form of anhydrous sulphate, provided it is not heated to too high a temperature.

In their experiments, the solution of the manganous chloride was introduced into a weighed platinum crucible, and after adding a slight excess of sulphuric acid, the water was removed by heating on the water bath. The crucible, supported by a porcelain ring, was then inserted in a porcelain crucible in such a manner that there was a space of about 1 cm. between the platinum crucible and the outer crucible, the latter being heated over a strong bunsen flame until the contents of the inner crucible were quite dry. The results quoted prove the accuracy of the process.

If it is desired to weigh the manganese as manganosomanganic oxide, the residue should be treated with nitric acid, and the crucible heated in the upper part of the flame of a strong bunsen burner, in such a manner that an oxidising flame covers nearly the entire wall of the crucible. For accurate work, the weighing as sulphate is, however, preferable. L. DE K.

Estimation of Manganese separated as Carbonate. By MARTHA AUSTIN (*Amer. J. Sci.*, 1898, 5, 382—384).—The author confirms the statement of Guyard, that manganese may be completely precipitated by ammonium carbonate even in the presence of excess of ammonium chloride. Precipitated in this manner, the solution being heated to boiling, the precipitate is, of course, quite free from alkali salts, and may be converted by ignition into oxide, or, better still, weighed as sulphate (see preceding abstract). Attempts to weigh the carbonate as such were unsuccessful. L. DE K.

Volumetric Estimation of Iron in Hydrochloric Acid Solution by means of Potassium Permanganate. By M. HAUFFE (*Chem. Zeit.*, 1897, 21, 894—895).—The following reagents are required. A solution of potassium permanganate representing about 0.005 gram of iron per c.c.; an acid solution of manganous sulphate, made by dissolving 100 grams of the crystallised salt in 1300 c.c. of water and adding 200 c.c. of sulphuric acid; a cold saturated solution of mercuric chloride, and a dilute solution of stannous chloride.

The substance is dissolved in hydrochloric acid; any insoluble matter is, if necessary, fused with potassium sodium carbonate, and

the melt is then again boiled with hydrochloric acid. To completely destroy organic matter, the liquid is mixed with potassium permanganate and thoroughly boiled. When cold, the whole is made up to a definite bulk, and an aliquot part is taken for the titration. This is diluted to about 200 c.c., boiled, and stannous chloride added until the iron is completely reduced, any great excess being avoided; 100 c.c. of the mercury solution is now added, which should give a small but decided precipitate of calomel, and then 60—100 c.c. of the manganese solution. The liquid is rapidly cooled and titrated with the permanganate; the latter should be standardised in the same way, using pure iron wire for that purpose. L. DE K.

Determination of the Reducibility of Iron Ores. By JOHAN G. WIBORGH (*Chem. News*, 1898, 78, 4—6). Compact ores are less readily reduced by the carbon and carbonic oxide in the blast furnace than other ores, and the peroxide of iron is more easily reduced than less oxidised ores. As ordinary chemical analysis does not indicate how an ore will behave in the blast furnace, the author has devised an apparatus to test this factor. In it a vertical reduction tube, 1·6 metres long and 50 mm. in diameter, with a portion 35 mm. in diameter at the bottom, is suspended, 0·25 metre from the hearth, in a circular producer in which charcoal is burnt in a grate without forced draught. The temperature in this tube varies from 400° at 0·5 metre to 880° at 1·5 metres from the top, whilst the gas produced contains from 3·2 to 3·6 per cent. of carbonic anhydride and 30 to 32 per cent. of carbonic oxide, but when the tube is raised by 0·35 metre from the furnace there is 17 per cent. of carbonic anhydride. In this apparatus, reduction tests may be made by exposing samples of pulverised ore to high temperatures, gradually or suddenly, and in any quantities, but conveniently 8 to 10 grams in a wire gauze boat; one or many at a time may be tested. The author's practice is to suspend the boat in the 400° zone, the zone of dissociation of the reducing gas, for an hour, then to lower it directly into the hottest part of the tube, and after an hour to cool it in a current of carbonic oxide. In the product, the carbon, total iron, and metallic iron are determined, and also the proportion (in units per cent.) that the oxygen found after reduction bears to the amount of oxygen that would be found if the whole of the iron was present as peroxide, the last factor being called the degree of oxidation. The carbon is determined in Särnström's apparatus by oxidising with chromic solution and absorbing the carbonic anhydride; the metallic iron by treatment with sulphuric acid and measuring the hydrogen evolved; the total iron by dissolving 0·25 gram in hydrochloric acid, filtering, evaporating with sulphuric acid, dissolving in water, reducing with zinc, and titrating; the degree of oxidation by treating 0·4 gram of the sample with 5 c.c. of 10 per cent. sulphuric acid with agitation until the evolution of gas ceases, then warming with about 5 c.c. of sulphuric acid, sp. gr. = 1·23, until all the iron is dissolved, and titrating the solution with permanganate. In the case of refractory ores, the first solution is separated and the undissolved residue alone treated with a more concentrated acid, the solutions being mixed for the titration. The numbers obtained by these various iron determinations furnish

data for the calculation of the degree of oxidation, which for iron peroxides is 100; for the magnetic oxide, 88.9; and for the suboxide, 66.7.

D. A. L.

Separations with Alkali Chromates. By HARRY BREARLEY (*Chem. News*, 1898, 78, 14—16. Compare this vol., ii, 460).—*Separation of Iron and Aluminium.*—In solutions saturated with dissolved hydroxide, or in hot solutions containing free acetic acid, 0.5 gram of iron is precipitated by 10 c.c. of a solution containing 12.5 grams of potassium chromate per litre, whereas in the first case aluminium is only partially precipitated by 50 c.c. of the chromate solution, and in the second case it is not precipitated at all; when, however, both metals are present in a solution, the iron is only precipitated by a much larger quantity of chromate and carries aluminium with it, so that the reaction cannot be adopted as a means of separation; this appears to be due to the fact that ferric chloride dissolves freshly precipitated basic aluminium carbonate, and aluminium chloride dissolves freshly precipitated ferric hydroxide. In solutions where only the free acid of a solution of iron and aluminium salts has been neutralised without forming dissolved hydroxide, the aluminium is not precipitated at all by the chromate, whilst the iron is only imperfectly precipitated. The *separation of iron and chromium* can also not be effected in solutions saturated with hydroxide. The *separation of iron and nickel* in such solutions by means of potassium chromate is good in the absence of acid, and practically perfect in the presence of 1 per cent. of acetic acid, and inasmuch as a large excess of the precipitant may be used without injurious effect, the separation is good even in the presence of aluminium, which latter may be retained in solution by tartaric acid in the subsequent cyanometric estimation of the nickel, a point, however, to be considered later by the author; but in preparing the solution for this estimation it is necessary in the presence of chromic acid to add ammonium sulphate first, and then to render alkaline with ammonia. The ammonium sulphate prevents the formation of a basic nickel chromate and also heightens the silver iodide turbidity. The *separation of iron and copper* by the chromate is even better than in the case of the nickel, and in both instances the chromate surpasses the acetate separation. The separated copper may be easily estimated by the soda-cyanide process (this vol., ii, 140, 258).

D. A. L.

The Iodometric Estimation of Molybdenum. By FRANK A. GOOCH and JOHN T. NORTON, jun. (*Amer. J. Sci.*, 1898, 6, 168—175).—Friedheim and Euler having taken exception to the criticisms passed on their process by Gooch and Fairbanks (*Abstr.*, 1897, ii, 76), the authors state that, unless precautions are taken to exclude air, the results cannot be trustworthy. The apparatus is made by sealing a separating funnel on to a 100 c.c. Voit distilling flask; this is in turn connected with a Drexel wash-bottle, placed in cold water and containing solution of potassium iodide. To prevent even the slightest escape of iodine, it is fitted with a bulbed trap. About 0.3 gram of the molybdic acid and 0.75 gram of potassium iodide having been introduced into the distilling flask, the air is expelled by means of a

current of carbonic anhydride, generated in a Kipp's apparatus from marble and hydrochloric acid containing some cuprous chloride. Forty c.c. of hydrochloric acid of 1.12 sp.gr. is then introduced by means of the separating funnel, and the whole is gently boiled in a current of the gas until exactly 10 c.c. of liquid is left in the distilling flask, when it may be assumed that the last traces of iodine have been expelled. The liberated iodine is then titrated with standard solution of sodium thiosulphate as usual.

L. DE K.

Estimation of Technically Available Molybdenum in Molybdenite. By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1898, 37, 438).—About a gram of the mineral is digested (in a conical flask), for about 2 hours, with 25 c.c. of concentrated nitric acid; ammonia is then added, and the liquid filtered. The undissolved portion is treated with acid a second time, and the united filtrates evaporated to dryness with excess of nitric acid; the residue, consisting of molybdic acid and ammonium nitrate, is then treated with 50 per cent. alcohol, in which the latter alone dissolves. The molybdic acid may be collected and weighed, or better, dissolved in 50 c.c. of normal ammonia, and the excess of ammonia titrated back with normal sulphuric acid. The metallic molybdates in the ore, which are technically useless, escape estimation. M. J. S.

Patera's Method of Estimating Uranium. By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1898, 37, 436—437).—The method, as given in Fresenius's *Anleitung zur quantitativen Analyse*, consists in dissolving the ore in nitric acid, adding an excess of sodium carbonate, boiling, and filtering, by which means the uranium passes into the filtrate with only traces of other metals, and can be thrown down by sodium hydroxide as sodium uranate. This method gives fairly accurate results with rich ores, such as pitch blende, but when applied to poor ores the precipitate is liable to be seriously contaminated with silica. It is therefore advisable to dissolve it in hydrochloric acid (after igniting) and to precipitate the uranium by ammonia from the filtrate. This precipitate is more easily washed than that with soda, and after ignition is weighed as U_3O_8 .

M. J. S.

Estimation of Tin in Tin Salts. By A. FROENKEL and J. FASAL (*Chem. News*, 1898, 78, 100—101).—The solution of the tin salt containing 0.2 to 0.4 gram of metal is treated in a flask with a few drops of hydrochloric acid along with from 0.5 to 1 gram of aluminium wire and gently heated. In about half an hour, when the tin is all precipitated, both metals are completely dissolved by heating with 10 c.c. of concentrated hydrochloric acid; the solution is rendered alkaline by sodium hydrogen carbonate and Rochelle salt, and then titrated with iodine. The results are low.

D. A. L.

Detection of Bismuth. By EGIDIO POLLACCI (*Gazzetta*, 1898, 28, i, 391—394).—Bismuth compounds containing bromine or chlorine colour the bunsen flame bright green; the iodide, oxide, or other bismuth compounds do not give this colour.

W. J. P.

Analysis of Soils. By MAX PASSON (*Zeit. angew. Chem.*, 1898, 777—781).—The author has slightly modified the process recommended by Dyer (*Trans.*, 1894, 115), and operates as follows: 120 grams of the dry soil is introduced into a litre flask containing 600 c.c. of a 2 per cent. solution of citric acid, and after the lapse of half an hour it is shaken for half an hour in a Wagner's apparatus. The liquid is then filtered and 100 c.c. is taken for the estimation of the potassium. This, after adding a few drops of phenolphthalein, is mixed with a slight excess of barium hydroxide, which precipitates the greater part of the citric acid; basic lead acetate may also be used, but baryta is better. The excess of barium, or lead, is precipitated by ammonium carbonate, and the liquid is then made up to 250 c.c.; 100 c.c. of the filtrate, representing 8 grams of the soil, is evaporated in a platinum dish, the residue incinerated until the carbon is almost entirely burned away, and then powdered and boiled with dilute hydrochloric acid, the whole being evaporated to dryness. After gently igniting the residue, it is dissolved in water, filtered, and precipitated as usual with platinic chloride.

Lime is best estimated by treating the earth in a litre-shaking flask for half an hour with 500 c.c. of standardised hydrochloric acid containing about half a per cent. of hydrogen chloride, and titrating an aliquot part with soda, using phenolphthalein as indicator.

L. DE K.

Contributions to Forensic Chemistry. [Detection of Phenol, Benzaldehyde, Carbon Bisulphide, Picrotoxin, Coniine and Nicotine]. By H. MELTZER (*Zeit. anal. Chem.*, 1898, 37, 345—358).—*Detection of Phenol and Benzaldehyde.*—On heating to boiling an aqueous solution containing both phenol and benzaldehyde mixed with twice its volume of concentrated sulphuric acid, it becomes deep red, and (if not too dilute) gives a red, resinous deposit. On adding potash (after cooling) to alkaline reaction, the resinous substances dissolve with fine violet-blue colour, and if the liquid, after acidifying, is shaken with ether, the colouring matter dissolves in it; on evaporation, a residue is left which dissolves in dilute alcohol and is coloured blue by alkalis, but is colourless in presence of free acids. Half a milligram of phenol and one drop of benzaldehyde suffices for the reaction.

Detection of Carbon Bisulphide.—Carbon bisulphide, treated with alcoholic potash, is converted into potassium xanthate, which, when boiled for a short time with ethylic iodide, yields diethylic thiocarbonate; as this, when boiled with ammonia, splits up into ethylic thiocarbamate and mercaptan, the latter by its odour affords a means of recognising carbon bisulphide, even when no more than two milligrams is present. The ethylic thiocarbamate can also be recognised, since on boiling with alcoholic potash it is converted into potassium thiocyanate which can be detected by its reaction with ferric salts.

Another method consists in passing the vapour of carbon bisulphide along with carbonic anhydride over fused potassium cyanide, which is thereby converted into thiocyanate. A tube containing lead acetate

should be inserted in the series to arrest any hydrogen sulphide. Five milligrams of carbon bisulphide can be detected in this way, but the method is, of course, open to the objection that all volatile sulphur compounds produce the same result.

Detection of Picrotoxin.—A trace of picrotoxin treated with benzaldehyde (diluted with its own volume of alcohol to diminish the yellow colour which it gives with the sulphuric acid) and a drop of concentrated sulphuric acid acquires a red colour, which, on gentle stirring, forms red streaks through the liquid.

Detection of Coniine and Nicotine.—An alcoholic solution of coniine mixed with carbon bisulphide acquires a yellow colour, nicotine gives no coloration. On adding to the yellow solution a few drops of a dilute solution of copper sulphate (1:200) or ferric chloride, characteristic yellow to brown precipitates are produced; nicotine gives no such precipitate, although with larger quantities of the metallic salts it yields feeble yellow colorations. The brown copper precipitate is completely removed by ether (after adding water). Lobeliine, aniline, and methylamine give feeble yellow colours with carbon bisulphide, but whereas these colours are no longer visible at dilutions of 1:500, coniine gives a distinct reaction at a dilution of 1:10,000. On dissolving a trace of nicotine in epichlorhydrin and heating to boiling, a deep red coloration is produced, whereas coniine gives no coloration; about 0.00025 gram of nicotine can be thus detected. Strong solutions of lobeliine give a similar colour, but dilute solutions give only a feeble yellow. Aniline, dimethylamine, cadaverine, and ammonia do not produce any coloration. M. J. S.

Characteristic Reaction of Cane-sugar. By G. POPASOGLI (*Ann. Agron.*, 1898, 24, 141; from *Bull. Assoc. Chim. Sucr. Dist.*, 13, No.1), —When 0.5 c.c. of a 5 per cent. solution of a cobalt salt and 5 c.c. of 50 per cent. soda solution are added to a 10 or 20 per cent. solution of saccharose, a stable amethyst coloration is produced. In the case of glucose, a blue colour is obtained, which soon becomes greenish. The two sugars are readily distinguished, and it is possible to recognise the presence of a tenth of saccharose in glucose, and to detect addition of cane-sugar to wine, condensed milk, &c. Honey gives a blue colour which changes to pale green; lactose gives an unstable blue. Substances to be examined should be freed from dextrin and gum by means of baryta and lead subacetate.

According to Beeson, a slight quantity of saccharose, in presence of much glucose, gives the blue coloration of glucose in reflected light, whilst in transmitted light, at a distance of about 80 cm. from the eye, the violet colour of saccharose can be seen (*Exp. Stat. Record*, 7, 740). N. H. J. M.

Estimation of Starch in Cereals. By CARL J. LINTNER (*Zeit. angew. Chem.*, 1898, 725—729).—This is an investigation as to the best methods of estimating starch in cereals. The final conclusions are: 1. The various methods in use all give different results, and an analyst should, therefore, state what process he has employed. 2. The substances which interfere are the pentosans. 3. When these are duly allowed for, the results obtained by various operators agree more

closely. 4. The best process will be, no doubt, the method proposed by Sachsse:—dissolving and inverting the starch in one single operation, making due allowances for the dissolved pentosans.

L. DE K.

Detection of Sawdust in Meal. By G. A. LE ROY (*Compt. rend.*, 1898, 126, 1047—1048).—When an alcoholic solution of phloroglucinol strongly acidified with phosphoric acid is added to meal and gently heated, any particles of sawdust that may be present acquire an intense carmine-red colour, whilst fragments of grain are but slightly affected and starch remains colourless. A hydrochloric acid solution of phloroglucinol acts too energetically, and the difference between the wood cellulose and the grain cellulose is not sufficiently distinct.

C. H. B.

Estimation of the Acidity of Urine. By CHARLES LEPIERRE (*Compt. rend.*, 1898, 126, 1534—1536).—The author discusses the various methods that have been proposed for the estimation of the acidity of urine. He considers that the only exact method is that of Gautier, in which the liquid is made alkaline by means of standard sodium hydroxide solution, the phosphates and other salts precipitated by barium chloride, and the residual alkalinity determined in an aliquot part of the filtered liquid, using phenolphthalein as an indicator.

If this method is combined with the determination of the acidity by means of sodium hydroxide in presence of barium chloride and phenolphthalein without previous filtration, it is possible to determine the respective quantities of monometallic and bimetallic phosphates present.

C. H. B.

Estimation of Tartaric Acid in Presence of Citric Acid. By ARTHUR BORNTÄGER (*Zeit. anal. Chem.*, 1898, 37, 477—485).—To ascertain how far the process worked out by Warrington and Grosjean (this Journ., 1875, 973; and Trans., 1879, 341) and investigated by the author (Abstr., 1886, 1082; 1887, 341), is suitable for the estimation of tartaric acid when citric acid is also present, mixtures containing 0.5 to 4 grams of hydrogen potassium tartrate with 0.5 to 5 grams of citric acid and 5 grams of potassium chloride were neutralised whilst hot by potash, cooled, made up to 50 c.c., and 6 c.c. of a 50 per cent. solution of citric acid added, stirred until a precipitate appeared, and left until the next day before filtering. The precipitates were washed with a 10 per cent. solution of potassium chloride saturated with hydrogen potassium tartrate, and finally twice with potassium chloride alone before titrating.

It was found that the mixture of 0.5 gram of tartrate and 5 grams of citric acid gave, under these conditions, no precipitate, but that a precipitate appeared when an additional gram of citric acid was added. In the cases where the citric acid originally present did not amount to more than twice as much as the tartrate, the use of 5 grams of citric acid as the precipitating agent gave fairly close quantitative results, but when the amounts of tartrate and (original) citric acid were about equal, 3 grams of citric acid sufficed for the precipitation.

The following rule is therefore laid down; such a quantity of the

mixture is to be taken as corresponds in total acidity with 3 grams of citric acid. It is neutralised, &c., as above, and precipitated with 3 grams of citric acid. Should the amount of tartrate found be more than double that of the citric acid found, the operation must be repeated with the addition (to the original mixture) of enough citric acid to restore approximate equality. Should, on the other hand, the amount of tartrate found be less than half the citric acid found, equality must be restored by adding a weighed quantity of tartrate.

M. J. S.

Polarimetric Estimation of Gallotannic Acid. By R. F. WOODSMITH and CECIL REVIS (*Analyst*, 1898, 23, 33—35).—The process, which is intended for the estimation of gallotannic acid only, but which may, perhaps, be also extended to other kinds of tannin, is based on the fact that, under certain conditions, gelatin forms with tannin a precipitate of definite composition. Consequently, if a solution of gelatin be polarised before and after treatment with tannic acid, the difference in the two rotations will serve as an indication of the amount of tannin.

The details of the process are as follows: 25 c.c. of a 9 per cent. solution of *gold label gelatin* in water at 45° is put into a 100 c.c. evaporating dish and heated on the boiling water bath to 60°; 1 c.c. of soluble albumin is then added, and the whole heated for 10 minutes with constant stirring. After cooling to 50°, it is again heated to 100° and filtered; the precipitate is washed with boiling water and the filtrate made up to 50 c.c. at 45°. The liquid, which must be perfectly transparent, is now examined in a Schmidt and Haensch polarimeter at 45°.

Twenty-five c.c. of the same gelatin solution is now heated with tannin solution containing about 0.6 gram of gallotannic acid, and the liquid poured off into another dish, the precipitate being washed with boiling water. The turbid liquid is clarified as before with fresh white of egg, and then again polarised. Each degree difference in polarisation (sugar units) represents 0.0673 gram of tannin.

L. DE K.

Detection of Cotton-seed Oil, Sesamé Oil, and Earth-nut Oil in Olive Oils. By MASSIMO TORTELLI and R. RUGGERI (*Zeit. angew. Chem.*, 1898, 850—853).—The authors (this vol., ii, 465) have devised a process for the detection of cotton-seed oil in edible oils; and they now extend this method to the detection also of sesamé or earth-nut oil. To detect sesamé oil, 5—6 c.c. of the liquid fatty acids is shaken with an equal bulk of strong hydrochloric acid and 2 drops of a 1 per cent. alcoholic solution of furfuraldehyde. Even if only 1 per cent. of the adulterant is present, it gives a characteristic carmine-red colour to the acid.

To test for earth-nut oil, the insoluble lead soap is first thoroughly exhausted with ether, and then shaken with this solvent in the presence of dilute hydrochloric acid. The ether is distilled off, and the residue of fatty acids is dissolved in 100 c.c. of 90 per cent. alcohol containing a drop of dilute hydrochloric acid, and the whole is heated to 60°. After cooling to 10—20° for about 3 hours, the crystalline precipitate

of lignoceric and arachidic acids is filtered off and washed, first three times with 10 c.c. of 90 per cent. alcohol, and then several times with alcohol of 70 per cent.; it is then dissolved off the filter by boiling absolute alcohol, and to the filtrate is added 100 c.c. of 90 per cent. alcohol and a drop of weak hydrochloric acid; after heating to 60°, the whole is allowed to cool for 3 hours. The crystals are washed as before, and, finally, redissolved in boiling absolute alcohol. After evaporating the solvent, and drying the fatty acids at 100°, the melting point is taken; if this is between 74° and 75·5°, it indicates the presence of earth-nut oil. The percentage divided by 0·048 represents the amount of the adulteration.

L. DE K.

Oxidised Cotton-seed Oil, and a General Method for the Analysis of Oxidised Oils. By WILHELM FAHRION (*Zeit. angew. Chem.*, 1898, 781—785).—This is a study of the changes which take place in the constitution of cotton-seed oil when exposed to the air.

The experiments were made by saturating with cotton oil two pieces of wash-leather, previously exhausted with light petroleum, and then exposing them for 8 and 12 days respectively to the air. The first piece was exhausted with light petroleum, which was then evaporated; the second one was similarly treated, but yielded a further supply of fatty matter when again exhausted with ether. The three products thus obtained, on evaporation of the solvents, were then analysed, together with the original oil. The method employed was as follows. After taking the iodine, saponification, and acidity numbers as usual, 2 or 3 grams of the sample was saponified with 10 c.c. of 2N alcoholic soda, the alcohol evaporated, and the soap dissolved in hot water. It was then placed in a separating funnel, and decomposed with hydrochloric acid, 25 c.c. of light petroleum added, and, after thoroughly shaking, the whole was left over-night, when the clear aqueous liquid was drawn off, and the petroleum poured off from the undissolved sticky, oxidised fatty acids, the latter being slightly washed with more light petroleum. The residue left on evaporating the petroleum was weighed, dissolved in 25 c.c. of strong alcohol, titrated with N/2 soda, using phenolphthalein as indicator, and then shaken with light petroleum to dissolve the unsaponifiable matters. The oxidised acids are dissolved in hot alcohol, which is then evaporated in a weighed dish, allowance being made for any mineral matter which may be present. By deducting from the petroleum residue the weight of the unsaponifiable matter, the proportion of non-volatile acids is obtained, the molecular weight of which can be calculated from the amount of soda used. The weight of the total petroleum residue, *plus* that of the oxidised fatty acids, represents the *Hehner* number. It appears that, as the oxidation proceeds, the iodine figure gets very low, being 108·8 in the original sample, and only 55·4, 46·3, and 29·1 in the others; the *Hehner* figure also fell from 94·22 to 85·34, 83·62, and 74·20, and the non-volatile acids from 92·85 to 63·53, 62·91, and 35·76. The inner saponification figure fell from 186·9 to 128·8, 128·9, and 74·4. The amount of unsaponifiable matter fell from 1·1 to 0·72 in the last sample, but showed a slight apparent increase in the others. The molecular weight of the non-

volatile acids fell from 278.1 to 276.2, 273.2, and 269.1. On the other hand, the acidity figure rose from 2.2 to 13.3, 13.8, and 33.4; the total saponification figure from 190.4 to 223.1, 227.5, and 271.3; and the oxidised fatty acids from 0.27 to 20.70, 19.43, and 37.72. The melting points of the non-volatile acids rose from 35—36° to 45—46°, 46°, and 51°.

When cotton-seed oil is oxidised by means of alkaline potassium permanganate, a large quantity of volatile acids, chiefly butyric, is obtained.

L. DE K.

A New Method of Estimating Fat in Food, Flesh, Fæces, &c. By LEO LIEBERMANN and SALOMON SZÉKELY (*Pflüger's Archiv.*, 1898, 72, 360—366).—The substance to be investigated is boiled with potassium hydroxide; alcohol is added, and then sulphuric acid carefully. After cooling, the mixture is extracted with light petroleum, the soap dissolved in the light petroleum is determined, and the fatty acids estimated by titration with decinormal alcoholic potash. Full details of quantities used and formulæ for calculating the fat are given. The method is rapid, can be used with various forms of food-stuff, and gives results which closely approximate to the amounts found by the older method of ether extraction

W. D. H.

Fat Estimation by Liebermann's Saponification Method. By FERENCZ TANGL and J. WEISER (*Pflüger's Archiv.*, 1898, 72, 367—369).—The method, the principle of which is given in the preceding abstract, was compared with Dormeyer's gastric digestion method; flesh and fæces were examined. The numbers came out approximately the same; on the average, the new method gives slightly higher results. The main advantage of the new method is its rapidity.

W. D. H.

Official Instructions for the Examination of Fats and Cheese (*Zeit. anal. Chem.*, 1898, *suppl.* 7—30).—These official instructions, published on April 1st, 1898, by the Imperial Chancellor, prescribe in minute detail the mode of sampling and of carrying out the following analytical operations. Estimation in butter, margarine, lard, and other fats and oils, of the amounts of water, casein, milk-sugar, total ash, chlorine, &c.; detection of boric and salicylic acids, formaldehyde, artificial colouring matters, sesame, cotton seed, and other vegetable oils (by the phytosterol reaction); determination of the melting and solidifying temperatures of the fats and fatty acids, of the refractive index with the Zeiss refractometer, of the acid number, Reichert, Meissl, Köttstorfer, Hehner, and Hübl values, the non-saponifiable constituents, &c. In the case of cheese, the estimations of water, fat, total and soluble nitrogenous constituents, free acids and mineral constituents, and the procedure for ascertaining the origin of the fats present are described. The method of using the refractometer is very fully described, but it does not admit of serviceable abstraction apart from the illustrations given.

M. J. S.

Testing Colophony. By KARL DIETERICH (*Zeit. angew. Chem.*, 1898, 915—919).—The author considers a sample to be commercially pure if it conforms to the following tests. It should be transparent, and when boiled with water should only give the faintest

reaction with ferric chloride. It should leave practically no ash, and be entirely soluble in alcohol, oil of turpentine, ethereal oils, acetone, ether, chloroform, methylic alcohol, amylic alcohol, ethylic acetate, benzene, and carbon bisulphide; partially soluble in petroleum, the portion insoluble in light petroleum of low boiling point not to exceed 7 per cent. The acidity figure should vary from 145 to 185; the sp. gr. from 1·045 to 1·085.

The acidity is determined by dissolving 1 gram of the powdered sample in 25 c.c. N/2 alcoholic potash, allowing it to act for 2 hours in the cold; the excess of alkali is then titrated with N/2 sulphuric acid; no water should be added. The sp. gr. is conveniently determined by means of weak brines of sp. gr. varying from 1·070 to 1·085.

L. DE K.

Detection of Colophony in Dammar Resin. By EDUARD HIRSCHSOHN (*Zeit. anal. Chem.*, 1898, 37, 456—457; from *Pharm. Zeit. Russ.*, 31, 609).—The estimation of the acid number does not give trustworthy results in this case. Colophony is readily dissolved by aqueous ammonia (0·96), and is reprecipitated by acids; dammar resin yields a yellowish or reddish extract, which gives a feeble opalescence with acids. The resin is digested with the ammonia for half an hour, and the filtered extract acidified with acetic acid. Five per cent. of colophony can be detected.

M. J. S.

Detection of Colophony in Guaiacum Resin. By EDUARD HIRSCHSOHN (*Zeit. anal. Chem.*, 1898, 37, 459; from *Pharm. Zeit. Russ.*, 34, 513).—The method prescribed by the Russian Pharmacopœia consists in precipitating the resin by water from its alcoholic solution and shaking the precipitate with potash, when the guaiacum dissolves to a clear solution, whilst colophony gives a turbid solution and a precipitate of resin soap. The method may be applied directly to the original resin. The powdered substance is shaken with potash solution of about 15 per cent.; a stronger solution would precipitate the potassium salt of the guaiacum resin, whilst a weaker one fails to precipitate the colophony soaps. The presence of soda must be avoided. Another method is to shake the finely powdered resin with 4 or 5 parts of light petroleum, and mix the colourless filtrate with an equal volume of a 0·1 per cent. aqueous solution of cupric acetate. The presence of colophony is revealed by a blue or bluish-green colour. Should less than 10 per cent. be present, the petroleum solution would need concentrating.

M. J. S.

Detection of Pyramidone in Urine. By ADOLF JOLLES (*Zeit. anal. Chem.*, 1898, 37, 441—442).—Dimethylamidophenyldimethylpyrazolone, or pyramidone, prepared by Filehne and Spiro, and recommended by them as a substitute for antipyrin (*Berlin. Klin. Wochenshr.*, 1896, No. 48), yields bluish-violet colours when oxidised by ferric chloride, nitric and nitrous acids, and the halogens. Most of these colours rapidly fade and disappear, but the blue colour obtained with alcoholic iodine solution passes, after some time, into red. Hydrogen peroxide gives a blue colour only on warming; acidified permanganate acts too energetically, producing only colourless compounds. Of these reactions, that with iodine is alone suitable for detecting pyramidone

in urine. A 1 per cent. iodine solution floated on the urine (after 0.2 gram of pyrazolone had been taken twice a day) gave a sharp, violet-red ring, which, on standing, passed into reddish-brown.

M. J. S.

Detection of Quinine. By EGIDIO POLLACCI (*Gazzetta*, 1898, 28, i, 391—394).—The author detects quinine by the formation of thalleoquinine as follows. A centigram of the quinine compound is dissolved in 1 c.c. of water and 2 drops of sulphuric acid. A small piece of lead peroxide is then put in, and the liquid gradually heated to boiling; after adding 3—4 c.c. of water and allowing to stand, a layer of ammonium hydroxide is poured in, when an emerald green disc or ring is produced.

W. J. P.

Detection of Atropine and Hyoscyamine in Urine. By S. VREVEN (*Chem. Centr.*, 1898, i, 225; from *Pharm. Centr.-H.*, 1897, 38, 867).—Three hundred c.c. of the urine, after standing for 8 days, is made alkaline with ammonia, and after shaking with chloroform, the emulsion is drawn off and mixed with a little alcohol, which will cause the chloroform to separate; this is then shaken with acidified water, and the aqueous liquid is again made alkaline with ammonia and agitated with chloroform. Finally, the chloroform extract is evaporated, and the residue, dissolved in a drop of acidified water, is treated on a microscopic slide with a minute drop of a solution of 10 grams of potassium iodide, and 5 grams of cadmium iodide, in 100 c.c. of water (Marmé's reagent), and stirred until the milky liquid has become clear again. Crystals soon begin to form which, under the microscope, show very characteristic forms for either of the alkaloids.

L. DE K.

Application of the Digitonine Test. By C. C. KELLER (*Chem. Centr.*, 1898, i, 222; from *Ber. Deutsch. Pharm. Ges.*, 7, 470—471).—Kiliani having stated that digitonine does not occur in digitalis leaves, the author has repeated these experiments, and has come to the conclusion that Kiliani's digitaline was in reality digitonine.

If 0.01 gram of this alkaloid, dissolved in 5 c.c. of hydrochloric acid of sp. gr. = 1.19, is heated on the water bath, the liquid turns first yellow, then deep red, and finally dark blue. If, when cold, 20 c.c. of water is added, a blue liquid with a red fluorescence is obtained which soon diminishes. Of the other digitalis alkaloids, digitaline alone gives a somewhat similar reaction.

L. DE K.

Cubebs. By C. HARTWICH (*Arch. Pharm.*, 1898, 236, 172—199).—The author considers in detail the morphological characteristics of cubebs, and of fruits which are employed for their adulteration. It is pointed out that amongst the latter are fruits which contain no cubebin, and yet cannot be distinguished, either in appearance or microscopically, from true cubebs; as, however, they fail to yield a red coloration with sulphuric acid, owing to the absence of cubebin, an easy means is afforded for their detection.

W. A. D.

Detection of Albumoses in Urine. By IVAR BANG (*Zeit. anal. Chem.*, 1898, 37, 410—411); from *Deut. med. Woch.*, 1898, 17).—To avoid the disturbing effect of urobilin in testing for peptones with phosphomolybdic acid, 10 c.c. of the urine, to which, in a test

tube, 8 grams of finely powdered ammonium sulphate is added, is heated for a moment to boiling; the peptone adheres to the walls of the tube, and its separation is best promoted by centrifugalising for $\frac{1}{2}$ —1 minute. The upper liquid is decanted, the sediment washed with alcohol, which also is poured off and can be tested for urobilin, and the residue is dissolved in a little water, and, after filtration, tested for the biuret reaction. Other colouring matters in urine are without influence. Should the alcoholic extract be red and show the spectrum of hæmatoporphyrin, the urine may be first precipitated by barium chloride in order to remove that substance.

M. J. S.

Estimation of Proteids. By N. C. HENRIK SCHJERNING (*Zeit. anal. Chem.*, 1898, 37, 413—422).—This communication is mainly a summing up of the author's earlier papers on the same subject (Abstr., 1894, ii, 371; 1895, ii, 428; 1896, ii, 631; this vol., ii, 271, 416). The reagents used are those described in Abstr., 1896, ii, 631, with the addition of a 5 per cent. mercuric chloride solution, which is used instead of lead acetate when that reagent does not give satisfactory results. In all cases, the proteid solution should be so far diluted that 10 c.c. of it contains nitrogen corresponding with 5 c.c. of N/10 acid. If a quantity of the solution sufficient to require 10 c.c. of N/10 acid fails to precipitate all the iron from 0.8 gram of ferric acetate (Abstr., 1896, ii, 631), the substance is regarded as poor in ash, and calcium chloride or sodium phosphate is added prior to the precipitation with tin, lead, and iron respectively. In all cases, the precipitation takes place in an acid solution. The criterion of a satisfactory precipitation is that a clear filtrate containing (except in the case of ferric acetate) an excess of the reagent is obtained. After collecting the precipitates on an 11 cm. extracted filter, it suffices to fill the filter twice with the appropriate washing liquid; the iron precipitate alone requires 3—4 washings. The analytical numbers are finally worked out as follows: the stannous chloride precipitate (*a*) contains albumin I; the lead acetate or mercuric chloride precipitate (*b*) contains albumins I and II, and denuclein; the ferric acetate precipitate (*c*) contains the above with propeptones; the uranium acetate precipitate (*d*) contains peptone in addition to the others; and the magnesium sulphate precipitate (*e*) contains the two albumins and the propeptones. Thence a = albumin I; $b - [a + (c - e)]$ = albumin II; $c - e$ = denuclein; $c - b$ = propeptones; $d - c$ = peptones.

M. J. S.

Estimation of Gelatin. By P. CARLES (*Chem. Centr.*, 1898, i, 226; from *Rev. Intern. Falsif.*, 10, 203).—Jean has published a process for the estimation of gelatin in meat extracts based upon its precipitation by tannin and the estimation of the excess of the latter by titration with iodine.

The author points out that various kinds of gelatin combine with various quantities of tannin; for instance, 1 gram of tannin precipitates 1 gram of isinglass, 0.91 gram of gelatin, 0.87 gram of so-called Bordeaux-gelatin, and 0.80 gram of glue; also 31 grams of white of egg, 25 grams of blood-serum, and 3.10 grams of commercial albumin.

L. DE K.

Estimation of Indican in Urine. By AMANN (*Chem. Centr.*, 1898, i, 152; from *Rép. Pharm.*, 1897, 437).—Twenty c.c. of urine is gently shaken with a few drops of sulphuric acid, 5 c.c. of chloroform and 5 c.c. of a 10 per cent. solution of sodium persulphate; the indigo thus generated dissolves in the chloroform, colouring it a more or less deep blue. This reaction is more delicate than the oxidation by means of a hypochlorite, hypobromite, or permanganate, and is not interfered with by the presence of albumin. Scatole gives a reddish-violet coloration with the reagent, but the colouring matter does not pass into solution in the chloroform; the intensity of the colour corresponds with the amount of scatole. L. DE K.

Estimation of Urinary Indican. By EYVIN WANG (*Zeit. physiol. Chem.*, 1898, 25, 406—410).—The following method is recommended. The urine is precipitated with 20 per cent. solution of lead acetate, and the clear filtrate decomposed with the same volume of Obermayer's reagent. The mixture is then extracted with chloroform until the extract is colourless; the chloroform is evaporated, the residue dried on the water bath, and a few c.c. of concentrated sulphuric acid added; after 24 hours, 100 c.c. of water is added, and the liquid titrated with potassium permanganate. Various precautions to be adopted during the analysis are described fully. The author's results are reserved for a future paper. W. D. H.

Estimation of Indigotin on the Fibre. By A. BINZ and F. RUNG (*Zeit. angew. Chem.*, 1898, 904—905).—The authors think the following process is the best of all the methods as yet proposed. Ten grams of the cotton is boiled for 3 or 4 hours with 150 c.c. of glacial acetic acid in a Soxhlet's apparatus, and the acid is poured into 300 c.c. of water mixed with 150 c.c. of ether; the indigotin is completely precipitated, but remains suspended in the ethereal layer. The aqueous layer being removed by means of a separating funnel, the indigotin is collected on a weighed filter, washed with alcohol and ether, dried, and weighed.

Cellulose is also slightly dissolved by the acid, but the acetylated product remains dissolved in the ether. L. DE K.

Chemistry of Tobacco. By RICHARD KISSLING (*Chem. Zeit.*, 1898, 22, 1—4).—*Estimation of the Moisture.*—The moisture is best determined by first partially drying the sample over sulphuric acid; when dry enough to be powdered, it is weighed, and then reduced to a fine powder; 1 gram of this is then dried over sulphuric acid for 24 hours, when it will generally be quite dry. The dried tobacco is very hygroscopic, and, after 24 hours, will have reabsorbed nearly all its original moisture.

Estimation of Malic and Citric Acids.—The following method is proposed. Ten grams of the powder containing about 4 per cent. of moisture is put into a porcelain basin and thoroughly impregnated with 10 grams of dilute sulphuric acid; the mass is now mixed with about 10 grams of powdered pumice so as to obtain a reasonably dry mixture, which is placed in a filter paper cartridge and extracted for 20 hours with ether to dissolve the organic acids. The ether is then

diluted to 100 c.c., and extracted by being shaken with 100 c.c. of water saturated with ether, the extraction being repeated two or three times; the mixed aqueous solutions are diluted to 250 c.c., and 25 c.c. of this is warmed to expel the ether, and then titrated with standard baryta water; in this way, the joint amount of citric and malic acids is obtained. To find the amount of malic acid, the neutralised liquid is cooled to 0° , which causes the barium citrate to crystallise out; the precipitate is then washed with 20 c.c. of cold water, afterwards with 50 c.c. of a mixture of equal vols. of alcohol and ether, and the barium malate is completely precipitated by adding to the filtrate 160 c.c. of the same ether-alcohol mixture. The precipitate after being washed with a little ether-alcohol is dried and ignited, and from the amount of ash (barium carbonate) the amount of malic acid is calculated. The barium citrate precipitate is treated in the same manner.

L. DE K.

ERRATA.

VOL. LXIV. (ABSTR., 1893).

PART II.

Page	Line	
444	11	<i>for</i> “+ 58.1” <i>read</i> “- 58.1.”
445	4	„ “C ₃ H ₆ ” <i>read</i> “C ₃ H ₆ O.”

VOL. LXVIII. (ABSTR., 1895).

PART I.

381	22*	<i>for</i> “fenchone” <i>read</i> “fenchene.”
525	17*	„ “C ₇ H ₇ ·N:CH·CO·C ₇ H ₇ ” <i>read</i> “C ₇ H ₇ ·N:CH·CO·NH·C ₇ H ₇ .”

VOL. LXX. (ABSTR., 1896).

PART I.

464	13	<i>for</i> “two methylene hydrogen atoms by,” <i>read</i> “ketonic oxygen atom by two.”
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PART II.

INDEX.

723	16	Col. ii, <i>for</i> “carbides” <i>read</i> “borides.”
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* From bottom.

VOL. LXXIV. (ABSTR., 1898).

PART I.

- 26 11* for " $\text{NH} \begin{smallmatrix} \text{CMe:C(CN)} \\ \text{CMe:C(CN)} \end{smallmatrix} \text{NPh}$ " read
 $\text{"NH} \begin{smallmatrix} \text{CMe:C(CN)} \\ \text{CMe:C(CN)} \end{smallmatrix} \text{CHPh.}"$
- 45 5 and 6 ,, " $\text{au-dimethyloxalidine}$ " read " $\text{au-dimethyloxazolidine.}$ "
- 243 22 ,, " $\text{ethylallylthydantoin}$ " read " $\text{ethylallylthiohydantoin.}$ "
- ,, ,, " $\text{ethylphenylthydantoin}$ " read " $\text{ethylphenylthiohydantoin.}$ "
- 247 24 ,, " bromacetophone " read " bromacetophenone. "
- 253 2* ,, " $\text{COPh}\cdot\text{CO}\cdot\text{CH}_2\cdot$," &c., read " $\text{COPh}\cdot\text{CH}_2\cdot$," &c.
- 362 5* ,, " $\text{C}_6\text{HBr}(\text{NO}_2)_2\text{Ba}$ " read " $\text{C}_6\text{HBr}(\text{NO}_2)_2\text{O}_2\text{Ba.}$ "
- 423 23* ,, " $\text{methyloctylsulphonic}$ " read " $\text{methyloctylbenzenesulphonic.}$ "
- 444 2* ,, " $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{C} \\ \text{C}\cdot\text{NPh}\cdot\text{N} \end{smallmatrix}$ "
 $\text{read "C}_8\text{H}_{14} \begin{smallmatrix} \text{C} \\ \text{C}\cdot\text{NPh}\cdot\text{N} \end{smallmatrix} \text{C}\cdot\text{COOMe.}"$
- 476 $\left. \begin{matrix} 7^* \\ 5^* \\ 3^* \end{matrix} \right\}$,, " $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot$," &c., read " $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot$," &c.
- 490 9* delete "(this vol., i, 289).
- 512 21* for " ethylic " read " methyllic
- 530 18 ,, " TSCHEWSKY " read " ISCHEWSKY. "
- 582 11 ,, " Harries, C. " read " $\text{Harries, C., and F. Kaiser.}$ "
- 628 8 ,, " "628" " read " $\text{"654.}"$

PART II

- 75 11 for " Weissbach " read " Weisbach. "
- 91 15 ,, " $\text{some barium sulphate}$ " read " $\text{the barium sulphate.}$ "
- 124 19* after " Analysis " insert " $\text{by J. C. H. Mingaye.}$ "
- 299 10 & 12 ,, " dogfish " read " seal. "
- 382 2* delete " ZrSO_4 ,"
- 392 18 for " EUGEN LUDWIG " read " ERNST LUDWIG. "
- 397 2* ,, " Shieweck " read " Schieweck. "
- 437 19 ,, " Kubeite " read " Rubrite. "
- ,, 19* delete " Thorite. "
- ,, 17* for " at Cleveland " read " in Cleveland Co. "
- ,, 3* ,, " Columbia " read " Colombia. "
- 438 7 ,, " "29-23" " read " $\text{"29-28.}"$
- ,, 14* ,, " zircon with " read " $\text{zircons containing.}$ "
- 650 24* ,, " Meltzer " read " Melzer. "

INDEX.

- Page Col.
- 704 i, for " Niemantowski " read " Niementowski. "
- 756 ii, delete " Imperatorine " from List of Alkaloids.
- 858 ii, Line 2, for " oroselone " read " oreoselone. "

* From bottom.